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# A Summary of Oil Shale Activities at the National Bureau of Standards, 1975-1979

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Research and Development

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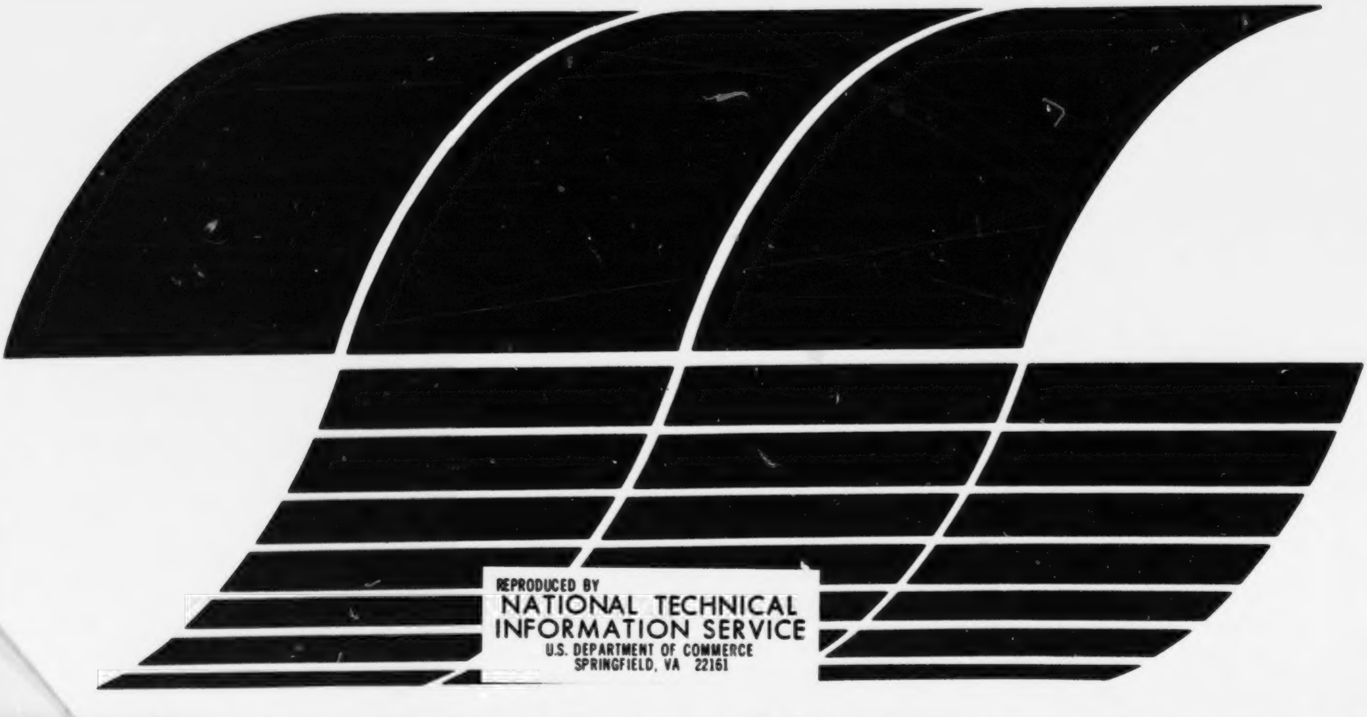
# A Summary of Oil Shale Activities at the National Bureau of Standards 1975-1979

## Interagency Energy/Environment R&D Program Report



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This report provides a summary of NBS Oil Shale activities covering the period 1975 to 1979. At the start of this period a Workshop on Standard Reference Materials (SRM's) needed for Oil Shale Processing was held at NBS and served to provide the priority guidance for the future of this program. A summary of the recommendations of that Workshop, the manuscripts presented during the Workshop, and the list of attendees is included in this report. The status of the Oil Shale Research at NBS is also presented consisting of developmental work on the feasibility of producing an Oil Shale and a Shale Oil Standard Reference Materials characterized for both trace inorganic and trace organic constituents. Additionally, information is given dealing with the development of measurement methods appropriate for Oil Shale and Shale Oil trace inorganic and trace organic analysis. Several papers are also included giving additional details on these matters. Other NBS Standard Reference Materials, which may be appropriate for the use by the Oil Shale community, are described briefly within this document. Finally, recommendations for future Oil Shale projects dealing with the development of measurement methods and Standard Reference Materials at NBS are presented.

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# A SUMMARY OF OIL SHALE ACTIVITIES AT THE NATIONAL BUREAU OF STANDARDS 1975 - 1979

Edited by

Lottie T. McClendon
Office of Environmental Measurements
National Bureau of Standards
U. S. Department of Commerce
Washington, DC 20234

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WASHINGTON, DC 20460

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# FOREWORD

The role of the National Bureau of Standards (NBS) in the Interagency Energy/Environment R&D program, coordinated by the Office of Research and Development, U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, State, local, and private industry participants in the entire program. The work at NBS is under the direction of the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry, The Center for Radiation Research and the Center for Thermodynamics and Molecular Science. NBS activities are in the Characterization, Measurement, and Monitoring Program category and address data quality assurance needs in the areas of air and water measurement methods, standards, and instrumentation. NBS outputs in support of this program consist of the development and description of new or improved methods of measurement, studies of the feasibility of production of Standard Reference Materials for the calibration of both field and laboratory instruments, and the development of data on the physical and chemical properties of materials of environmental importance in energy production. This report is one of the Interagency Energy/Environment Research and Development Series reports prepared to provide detailed information on the NBS measurement methods and standards development pertaining to Oil Shale activities. To provide a complete report on NBS Oil Shale activities this document contains summaries of research and development performed by NBS (parts of which were supported by the Interagency Energy/Environment Program and parts of which were supported by NBS directly appropriated funds and also funds obtained from other Federal agencies). The source of the funding used to support the various activities is so indicated in the appropriate places in this document. It is hoped that this document will provide those researchers involved in evaluating the environmental impact of increased Oil Shale production with information on measurement methods and Standard Reference Materials pertaining to data quality assurance in all aspects of their studies.

C. C. Gravatt, Chief
Office of Environmental Measurements
National Bureau of Standards

# ABSTRACT

This report provides a summary of NBS Oil Shale activities covering the period 1975 to 1979. At the start of this period a Workshop on Standard Reference Materials (SRM's) needed for Oil Shale Processing was held at NBS and served to provide the priority guidance for the future of this program. A summary of the recommendations of that Workshop, the manuscripts presented during the Workshop, and the list of attendees is included in this report. The status of the Oil Shale Research at NBS is also presented consisting of developmental work on the feasibility of producing an Oil Shale and a Shale Oil Standard Reference Materials characterized for both trace inorganic and trace organic constituents. Additionally, information is given dealing with the development of measurement methods appropriate for Oil Shale and Shale Oil trace inorganic and trace organic analysis. Several papers are also included giving additional details on these matters. Other NBS Standard Reference Materials, which may be appropriate for the use by the Oil Shale community, are described briefly within this document. Finally, recommendations for future Oil Shale projects dealing with the development of measurement methods and Standard Reference Materials at NBS are presented.

# ACKNOWLEDGMENT

The Office of Environmental Measurements, the National Bureau of Standards gratefully acknowledges the partial support of this work from the U.S. Environmental Protection Agency under the Interagency Energy/Environmental Agreement EPA-IAG-D5-E684. The Center for Analytical Chemistry of NBS gratefully acknowledges the support of the Department of Energy (Office of Health and Environmental Research) for the work described dealing with the development of methods for the quantitative determination of individual organic compounds in Shale Oil. Additionally, we acknowledge the considerable work of Mr. Donald Becker of NBS who was responsible for the initial planning and conduct of the Workshop on the needs for Standard Reference Materials for Oil Shale Processing.

# SECTION 1

# INTRODUCTION

The purpose of this report is to summarize the National Bureau of Standards' (NBS) activities in oil shale and oil-shale products. The role of NBS in oil shale research and development, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, state, local, and private industry participants in oil shale technology. Development of a compatible data base to assess the total effect of oil shale development upon our environment is a necessity if rational and logical decisions are to prevail in planning and developing this energy resource in an environmentally and economically acceptable manner.

A series of eight Workshops were conducted during 1975-1976 by the NBS and the Environmental Protection Agency to assess the needs and kinds of chemical standards and reference materials required for monitoring the environmental effects associated with energy development. The second workshop of the series was held November 24-25, 1975 at NBS. The objective of this workshop was to obtain input to NBS from pertinent experts on Standard Reference Materials, homogeneous intercomparison materials, and analytical methodology needed for the accurate analysis of environmental samples associated with oil shale processing. A summary of this workshop, recommendations made by the participants, as well as some of the papers presented on oil shale activities during the workshop are included as part 3 of this report. Part 4 of this report provides a summary of the oil shale research and development efforts performed at NBS over the past five years. The scope of work for ongoing and future oil shale projects are summarized in part 5.

# SECTION 2

# SUMMARY

The assessment of the environmental implication and impact of new and expanding energy techniques requires that an effective multimedia monitoring and measurement assurance system be maintained. Development of a compatible data base to determine the source, transport, and fate of environmental pollutants is a necessity if rational and logical decisions are to prevail in planning the types, pattern, and magnitude of energy developments which are environmentally acceptable. In recognition of this need, the Office of Management and Budget and the U.S. Congress established an Interagency Energy/Environment Research and Development Program in 1975 under the direction of the U.S. Environmental Protection Agency. This program established a mechanism for the planning, coordination, and allocation of research and development funds for environmental pollution control technologies associated with energy development.

As part of the Interagency Energy/Environment Program, an EPA/NBS interagency program was initiated in 1975. The overall objective of this program is to provide quality assurance for environmental baseline data in those geographical areas where the impact on the environment of energy development is or is projected to be of major magnitude. NBS activities within this program concern the development of measurement methods, Standard Reference Materials (SRM's) and instrumentation in support of programs for evaluating environmental effects of increased energy development. The measurement methods and SRM's developed at NBS will help to ensure comparability and compatibility among energy related measurements made in the laboratory and in field monitoring.

The 1973 Oil embargo spurred the National government to focus on the development of new energy technologies to meet our Nation's increased energy demands. One of the industries activated and spotlighted for technology development was the oil shale industry. By 1975, planning, design and environmental study efforts were underway on several oil shale tracts and the EPA had established a high priority Oil Shale program with two primary objectives: (1) support the regulatory goals of the Agency and (2) support and conduct research directed towards ensuring the oil shale industry develop in the most environmentally acceptable manner that was reasonably possible. However, with a short-lived oil embargo and very high construction costs, interest in developing the oil shale industry slackened in 1976 and 1977 and many Agencies reduced and/or directed priorities and funds from oil shale research and development to other areas and environmental issues. The NBS activity in oil shale has been in support of the objectives of other Agencies' oil shale programs (i.e. EPA, DoE) and as such, the NBS activity over the past five years has been impacted by the priorities and funding directives from such agencies.

The first major accomplishment of the NBS Oil Shale Program for the period 1975 to 1979 was a Workshop on Standard Reference Materials and Measurement Methods required for Oil Shale processing to develop priorities for the NBS activities in this program. It was concluded by that Workshop that raw Oil Shale, (the approximately 25 gallon per ton minus 200 mesh type) characterized for trace inorganic and trace organic constituents was the highest priority. Second priority was a processed shale material characterized for trace inorganic and organic constituents. The third priority was a research material shale oil, and forth priority was a research material process water. The second major accomplishment was the analysis of trace elements in oil shale from one pilot plant sample material. The third accomplishment was a comparison of gas chromatographic profiles before and after radiation sterilization of oil shale materials to ascertain the long-term stability of oil shale samples. The fourth was the development of measurement methods for an analysis of consent decree organics in shale oil based on high performance liquid chromatography techniques. Finally, feasibility studies were conducted on both the oil shale and shale oil materials in order to assess the production of these two materials as SRM's. The shale oil SRM material has been characterized for five trace organic constitutents and is expected to be available as SRM 1580 by April 1980. More work, as well as a shift in funds and priorities will be needed to characterize the shale oil for trace inorganic elements. The oil shale SRM is still under investigation due to the difficulty at the present time of certifying the complete extraction of organic compounds from the oil shale starting materials.

Future work at NBS is Oil Shale related activities will consist of the completion of the development of measurement methods required for certifying trace organic compounds in oil shale, thereby permitting the production of an oil shale SRM certified for trace organic constituents. Additionally, all commercial shale operations will be required to preserve water resources and to control effluent discharges. In order to meet those requirements, measurement methods and Standard Reference Materials will be needed for water discharge from oil shale operations. Similarly, process and fugitive emissions into the ambient air will require a variety of reference methods and Standard Reference Materials. The specific materials required will need to be determined after a careful analysis of the type of emissions found in pilot oil shale activities.

## SECTION 3

# SUMMARY OF WORKSHOP ON STANDARD REFERENCE MATERIALS FOR OIL SHALE PROCESSING

### a. Introduction

On November 24-25, 1975, a workshop (sponsored by EPA and NBS) was held at the National Bureau of Standards, Gaithersburg to determine the needs and types of Standard Reference Materials which could be used for monitoring the environmental effects of oil shale processing. Since the adequate evaluation of environmental pollution is based largely upon the results from chemical analysis, adequate reference materials are essential for quality assurance and inter-laboratory comparison purposes. Thus, the objective of this workshop was to obtain input to NBS from pertinent experts on certified reference materials, homogenous intercomparison materials, and analytical methodology needed for the accurate analysis of environmental samples associated with oil shale processing.

Several papers were presented during the workshop and many fruitful discussions took place on a variety of subject areas related to the environmental aspects of oil shale processing (e.g., trace inorganic, trace organic and gaseous pollutants, overview of environmental studies to that date and the significance thereof, etc.). As a result of a number of obstacles, the Proceedings of this Workshop were not published. Thus, three of the papers prepared for and presented during the Workshop are attached as Appendix A of the report (with author's permission).

### b. Purpose of Workshop - D. A. Becker

One of the purposes for this workshop involves what we can do to help you and how you can get information to us so we can miximize our return to you.

Accurate measurements in environmental monitoring is important since a 100% deviation in measurement can mean either over controlling or under controlling the process being monitored, both of which are undesirable.

NBS has three divisions involved in this program, the Office of Air and Water Measurement, The Office of Standard Reference Materials and The Analytical Chemistry Division.

What this workshop needs to discuss and determine includes the needs of the oil shale industry for reference materials, the elements needed and concentration levels involved, the requirement for organic analyses, the suitability of current methods and how best such needs can be met.

Priorities are needed from this workshop to determine what is to be done realizing that NBS had limitations on funds, people, and time.

### c. Workshop Summary

The following summary on the Oil Shale Processing Workshop covers the major recommendations made under four main material types considered as possible SRM's for oil shale operations: Raw Oil Shale; Spent Shale; Shale Oil; and Process Water.

#### Raw Oil Shale:

The priority requirement for an SRM, to be used in the oil shale processing field, was a powdered raw oil shale. Complete analysis of a raw oil shale SRM is needed to provide the foundation for batch production analyses and to assess the environmental impact, and the immediate focus would be trace elements. This material should come from the Mahogany zone oil shale, preferably Anvil Point, and contain approximately 25 gallons oil/ton. The material should be sterilized by Cobalt-60 radiation for stablility.

As in all grinding operations, the contamination by the grinding materials can be severe. After due consideration, it was recommended that alumina grinding balls be used if possible. The next best material would be hardened steel rather than tungsten carbide which would cause cobalt contamination. It was also pointed out that there was a need for care in shale grinding due to the possible degradation of the hydrocarbon components caused by the heating and oxidation that occurs during the grinding process. To minimize this problem, the material should be ground in an inert atmosphere.

A final SRM sample size of 80 to 100 grams would be sufficient for trace element use. Trace elements certified should include arsenic, selenium, boron, molybdenum, lead, zinc, mercury, flourine, antimony, cadmium, vanadium, cobalt, nickel, iron, uranium, thorium, chromium, lithium, and beryllium. Calcium, magnesium and other major elements should also be certified. In addition, carbon, hydrogen, nitrogen, sulfur, and total and organic carbon should be certified along with the moisture content. It was suggested that information on storage under refrigeration be included since organic decomposition would be minimized. Storage under refrigeration would also prevent the sample being left on the shelf where heat and light would speed up the decomposition process. Due to the usefulness of the Fischer Assay determination, it was suggested that an amount of the original material be split off at 60 mesh and used as a Research Material for Fischer Assay determinations.

Although not of the same matrix, the currently available SRM's for Coal (1632) and Fly Ash (1633) should be very useful in instrumental procedure development.

#### Spent Shale

The second priority requirement was for a spent shale SRM. To cover the present processes, two types of spent shale SRM's would be needed. One material from the oxidative process (Paraho) and the other from the reductive process (TOSCO II). The certification required for these materials would be the same as that described for the raw shale material. However, no information on Fischer Assay would be needed.

## Shale Oil

The third priority material was shale oil. Four source possibilities exist for a shale oil standard: TOSCO II, Paraho, Occidental and "in-situ." It is expected that considerable compositional differences would occur among these four types due to the differences in manufacture. The main analyses needed for shale oil could be confined to those elements that are catalyst poisons.

It is expected that the shale oil will go through a refining process to become standard petroleum products. As a result, the shale oil did not carry a high priority as a needed SRM, but it was recommended the oil be available as a Research Material.

## Process Water

The fourth priority material recommended in the workshop was process water. Since techniques are presently not available for certification analysis of organics in water, the production of a process water SRM was felt to be impossible at the time of the workshop. However, considerable need existed for the development of methods for trace organic analysis in effluents from shale oil processing.

Although the process water is alkaline, the soon to be released water SRM (At the time of this workshop, the Trace Element in Water SRM, 1643 was not available. Since that time, SRM 1643 was sold out and SRM 1643a is ready for re-issue) should suffice for trace element analysis. Individual laboratories would be required to modify the water SRM and test procedures for their elements of interest.

It was recognized that the determination of trace organics in water would become a serious problem as production increased and analytical methods would need to be developed in order to characterize process waters for organic constituents.

## d. Workshop Program

ENERGY/ENVIRONMENT WORKSHOP
SRM's FOR OIL SHALE PROCESSING
NOVEMBER 24-25, 1975

NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MARYLAND

November 24, 1975

Welcome - D. A. Becker, NBS

Introductory Remarks -
G. D'Alessio, EPA

Statement of Purpose -
D. A. Becker, NBS

Session I -

A. "Oil Shale Overview"
B. "Preparation of Standard Oil-Shale Samples OS-1, SS-1, and SS-2"

T. R. Wildeman
Colorado School of Mines

Session II -

C. "Environmental Studies"

T. R. Wildeman
Colorado School of Mines

"Determination of Trace Metals in Oil Shale, Materials Balance Studies"

M. T. Atwood
TOSCO

Session III -

"Environmental Effects of Organic Trace Elements in Oil Shale and Waste Products."

J. J. Schmidt-Collerus
Denver Research Institute

"Trace Elements in Oil Shale Liquid Products"

R. E. Poulson
ERDA, Laramie, WY

Session IV -

Open Discussion

Address

"NBS and Pollution"

J. R. McNesby
Office of Air and Water Measurements, NBS

November 25, 1979

Session V

"High Resolution Techniques for Analysis of Polycyclic Hydrocarbons"

E. L. Wehry
University of Tennessee

"Speciation"

J. Fruchter
Battelle Northwest Laboratories

Session VI - Brief Remarks

"ERDA's Role in Energy and Environment"

G. J. Rotariu
ERDA

"Use of Standard Reference Materials"

J. P. Cali
Office of Standard Reference Materials, NBS

Discussion

Session VII - Closing Discussion

## e. LIST OF ATTENDEES

### Energy/Environment Workshop

### SRM's for Oil Shale Processing

Mark Atwood
The Oil Shale Corporation (TOSCO)
18200 West Highway 72
Golden, Colorado 80401

I. Lynus Barnes
Analytical Spectrometry
National Bureau of Standards
Washington, DC 20234

Donald A. Becker
Analytical Chemistry Division
National Bureau of Standards
Washington, DC 20234

Francis Bonomo
Denver Research Institute
2390 So. University Boulevard
Denver, Colorado 80206

Irving Breger
Office of Energy Resources
U. S. Geological Survey
National Center, Stop 923
Reston, Virginia 22092

J. Paul Cali
Office of Standard Reference Materials
National Bureau of Standards
Washington, DC 20234

Stephen Chesler
Bioorganic Standards
National Bureau of Standards
Washington, DC 20234

Bruce R. Clark
Analytical Chemistry Division
Holifield-Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37831

Jack Clarkson, L-404
Lawrence Livermore Laboratories
P. O. Box 808
Livermore, California 94550

Richard H. Coe
Shell Development Co.
Westhollow Research Center
P. O. Box 1380
Houston, Texas 77001

Gregory D'Alessio
Office of Research & Development
Environmental Protection Agency
Waterside Mall - R/D 681
401 M Street, SW
Washington, DC 20460

Jon Fruchter
Battelle Northwest Laboratories
P. O. Box 999
Richland, Washington 99352

Donald B. Gilmore
Environmental Monitoring and Support Laboratory
Environmental Protection Agency
P. O. Box 15027
Las Vegas, Nevada 89114

Barry H. Gump
Bioorganic Standards
National Bureau of Standards
Washington, DC 20234

Harry S. Hertz
Bioorganic Standards
National Bureau of Standards
Washington, DC 20234

David Jones
Radian Corporation
Box 9948
Austin, Texas 78766

James R. McNesby
Office of Air and Water Measurement
National Bureau of Standards
Washington, DC 20234

Thomas W. Mears
Office of Standard Reference Materials
National Bureau of Standards
Washington, DC 20234

John A. Norris
Analytical Chemistry Division
National Bureau of Standards
Washington, DC 20234

Richard E. Poulson
ERDA-Laramie
Box 3395
University Station
Laramie, Wyoming 82070

Harry L. Rook
Activation Analysis
National Bureau of Standards
Washington, DC 20234

George J. Rotariu
Energy Research & Development
Administration
Washington, DC 20540

Robert Schaffer
Bioorganic Standards
National Bureau of Standards
Washington, DC 20234

Josef J. Schmidt-Collerus
Denver Research Institute
University of Denver
University Park
Denver, Colorado 80206

Haven Skogen
Occidental Oil Shale
P. O. Box 2999
Grand Junction, Colorado 81501

Charles Taylor
Southeast Environmental Research
Laboratory
Environmental Protection Agency
College Station Road
Athens, Georgia 30601

John K. Taylor
Air and Water Pollution Analysis
National Bureau of Standards
Washington, DC 20234

Howard Taylor
Accu-Labs Research, Inc.
11485 West 48th Avenue
Wheat Ridge, Colorado 80033

Earl L. Wehry
University of Tennessee
W. Cumberland Avenue, SW
Knoxville, Tennessee 37916

Thomas R. Wildeman
Department of Chemistry
Colorado School of Mines
Golden, Colorado 80401

# SECTION 4

## STATUS OF OIL SHALE RESEARCH AND DEVELOPMENT AT NBS

### a. Introduction

It has been long recognized that accurate baseline data and effective and meaningful monitoring programs are essential to understanding the environmental impact of an industry. Thus, NBS efforts in oil shale technology have been focused on developing measurement methods and standards to help ensure accuracy, comparability and compatibility amo g related measurements in the oil shale industry. The following discussion describe NBS activities on powdered oil shale and shale oil.

### b. Raw Oil Shale

As a result of the recommendation from the workshop on "SRM's for Oil Shale Processing" (Section 3 of the report), NBS obtained samples of oil shale from TOSCO (originated from Parachute Creek Area) and oil shale from the Energy Research Center at Laramie, Wyoming (originated at Anvil Points Area) in early 1976. In addition to the workshop recommendation, the experience obtained in producing the Coal and Fly Ash materials (i.e. SRM 1632 and 1633) for trace element certification provided the basis for NBS's initial focus on trace elements in the raw oil shale. The two oil shale materials were ground according to recommendations set forth at the workshop and prepared for the preliminary assessments required of a potential Standards Reference Materials (e.g., homogeneity, elemental profile, suitability.

Instrumental Neutron Activiation Analysis (INAA) was used to provide a preliminary assessment of the trace element concentration of minus 200-mesh TOSCO oil shale. The elemental concentrations observed are listed in Table 4-1 with the estimated analytical uncertainties which could be obtained. To conduct this study, the NBS SRM 1632 (coal) was used as the reference material. The NBS SRM 1633 (Fly Ash) was treated as an unknown sample material along with the oil shale material during the study for comparison purposes. Several oil shale samples have been semi-quantitatively analyzed using emission spectroscopy by NBS scientists in conjunction with work being performed for another NBS program. While the results are very preliminary using this technique some of the elemental concentrations obtained agree favorably with those obtained using INAA (e.g. Na,K, Fe, Cr).

A portion of the oil shale material was radiation-sterilized, analyzed for its trace element content by INAA, and the results obtained compared to the trace element concentration of the unsterilized oil shale to determine if there were changes in the elemental concentration of volatile elements. A preliminary interpretation of the results, indicated there were no significant elemental concentration differences in the two materials.

Additionally, high resolution gas chromatography was conducted on the unsterilized and the radiation sterilized oil shale. Extracts of the oil shale analyzed with or without cobalt-60 irradiation sterilization of the oil shale gave identical chromatograms. Evaluation of the organic extraction efficiency is needed to quantify organics present in the oil shale.

As a result of the trace element assessment, the TOSCO oil shale was chosen as the material to be used for production of the first trace element oil shale SRM. In June, 1978, NBS received a batch of processed TOSCO oil shale (about 1200 lbs.) to begin the certification process. However, by that time, the other agencies had directed its resources be used by NBS to support their other priority programs, The certification program for trace elements in oil shale is currently at a standstill. Method development for trace organic analysis is currently in progress and preliminary studies will be conducted on the TOSCO oil shale to assess the feasibility for its use as a trace organic SRM.

## TABLE 4-1

## Elemental Concentrations (μg/g unless indicated) and Estimated Uncertainties Attainable

|  | Oil Shale |  | SRM 1632* Coal | SRM 1633 Fly Ash |
|---|---|---|---|---|
| Na (%) | 1.6 | 5% | 0.040 | 0.34 |
| K (%) | 1.0 | 5% | 0.27 | 1.6 |
| Rb | 63 | 5% | 20 | 120 |
| Cs | 3.4 | 5% | 1.4 | 7.9 |
| Ba | 540 | 5-10% | 330 | 3100 |
| Sc | 4.6 | 5% | 3.7 | 27 |
| Cr | 32 | 5% | 20.2 | 120 |
| Fe (%) | 1.8 | 5% | 0.87 | 6.4 |
| Co | 9.0 | 5% | 5.6 | 40 |
| As | 64 | 5% | 5.9 | 62 |
| Se | 3.5 | 5-10% | 2.9 | 11 |
| Sb | 2.8 | 5-10% | 4.3 | 6.9 |
| La | 20 | 5% | 11.3 | 89 |
| Ce | 34 | 5% | 20.4 | 160 |
| Sm | 2.5 | 5% | 1.83 | 14 |
| Eu | 0.52 | 5% | 0.38 | 3.0 |
| Yb | 0.85 | 5% | 0.70 | 4.9 |
| Lu | 0.18 | 5% | 0.14 | 1.0 |
| Hf | 1.5 | 5-10% | 0.95 | 7.8 |
| Ta | 0.30 | 10-15% | 0.21 | 1.5 |
| Th | 4.7 | 5% | 3.0 | 25 |

* Reference Material Used for Calculation of the Oil Shale Values.

### c. Shale Oil

The potential carcinogenicity of processed oil shale and its products has received widespread attention in the press and is presently a primary concern of environmentalists. The determination of trace elements and trace organic compounds in very complex mixtures (e.g. processed oil shale, feedstock, process streams, plant effluents) is very difficult. Many of the analytical techniques that have been used in the past to characterize oils and effluents from petroleum technology are inadequate or cannot be applied to the characterization of oil shale materials. As a result, NBS's efforts have focused on developing measurement methods to accurately identify and quantify individual organic compounds in complex matrices. The certification of trace organic Standard Reference Materials for shale oil, liquified coal, etc. are contingent upon the development of accurate methods for quantifying individual toxic and/or carcinogenic compounds in such complex matrices.

NBS obtained a quantity of shale oil from Oak Ridge National Laboratory in 1978, to apply NBS developed methods and assess the feasibility of preparing a trace organic Shale Oil SRM. The results of these efforts are described (Sec. 4.d of this report) in the draft, "Methods for the Quantitative Determination of Individual Orgnaic Compounds in Shale Oil." In addition to the financial support from the EPA Interagency Energy/Environment Research and Development Program, the work described in this draft was performed with partial financial support from the Office of Health and Environmental Research of the Department of Energy. The authors of this draft are in the process of finalizing their work for publication. A Shale Oil SRM, 1580, certified for five polycyclic aromatic hydrocarbons (PAH)--pyrene, fluoranthene, benzo(a)pyrene, benzo(e)pyrene, o-cresol--will be available from the NBS Office of Standard Reference Materials by April 1980.

# d. Methods for the Quantitative Determination of Individual Organic Compounds in Shale Oil*

H. S. Hertz, J. M. Brown, S. N. Chesler, F. R. Guenther,
L. R. Hilpert, W. E. May, R. M. Parris, and S. A. Wise

Organic Analytical Research Division
National Bureau of Standards
Washington, DC 20234

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## Brief

Acid-base extraction and high performance liquid chromatography are used to fractionate shale oil. Capillary gas chromatography, high performance liquid chromatography and gas chromatography-mass spectrometry are used to identify and quantify individual compounds in the shale oil fractions.

# Abstract

Several techniques have been investigated for quantitating individual organic compounds in shale oil. Emphasis was focused on acid-base extraction and high performance liquid chromatography as independent methods of shale oil fractionation. Gas chromatography, gas chromatography-mass spectrometry and high performance liquid chromatography were used for individual compound quantitation utilizing external and/or internal standards or standard addition techniques. The following compounds were measured in the shale oil: pyrene, fluoranthene, benzo(e)pyrene, benzo(a)pyrene, phenol, *o*-cresol, acridine, and 2,4,6-trimethylpyridine. Comparable results were obtained by the various methods for extraction and quantitation.

Increasing energy demand in the United States and reliance on foreign sources of petroleum have resulted in a national program designed to develop new sources of energy. The conversion of coal to gaseous or liquid fuels and the utilization of oil shale and tar sands are some of the energy sources that appear promising. In terms of energy, it is estimated that domestic coal and oil shale reserves are $8000 \times 10^{15}$ and $400 \times 10^{15}$ BTU, respectively, while petroleum reserves are only $200 \times 10^{15}$ BTU (1). However a serious and still largely unknown complication of developing these alternate fuels is their potentially deleterious impact on man and the environment. To evaluate this impact properly, it will be necessary to analyze the feedstock, process streams, plant effluents and final product for their trace element and organic compound content. The accurate quantitative analysis of individual organic compounds will become increasingly important as mutagenicity testing on chromatographic fractions generated from various fuels and effluents expands. These tests should eventually allow scientists to relate health effects to known amounts of specific compounds.

One method for assuring the accuracy of the necessary quantitative analyses is the use of suitable quality assurance standards or Standard Reference Materials (SRM's). The certification of such trace organic SRM's is contingent upon the development of the analytical expertise to achieve individual compound quantitation in complex matrices such as shale oil, liquified coal, or petroleum. In the past many of the analytical techniques that have been used for the evaluation of synthetic oils have been taken from petroleum technology (2-4). These analyses generally involve an initial separation of the mixture into compound classes by solvent extraction techniques followed by various methods of further characterization. The procedures that have been used for further characterization were usually designed for the determination of physical and chemical properties of distillate fractions which are important to product characteristics but are not designed for individual compound identification and quantitation.

Recently several methods for the analysis of specific classes of compounds in samples of petroleum, shale oil and synthetic coal liquids have been reported. Jackson *et al* (5) determined hydrocarbon types in shale oil distillates by use of a hydroboration-acid adsorption technique; McKay and coworkers (6) utilized a chromatographic-infrared technique to characterize nitrogen bases in high boiling petroleum distillates. Uden *et al* (7) have characterized the acidic and basic fractions of shale oil by gas chromatography-Fourier transform infrared spectroscopy Popl *et al* (8) have used frontal elution on silica gel followed by adsorption chromatography on alumina and gel permeation chromatography to characterize polynuclear aromatic hydrocarbons (PAH) in white petroleum products. Suatoni and Swab (9) developed a "back-flush" high performance liquid chromatographic technique for the determination of total saturated and aromatic hydrocarbons from crude oils and synthetic crudes derived from coal. Several workers (e.g. 10) have recently applied mass spectrometry to class specific analysis of coal liquids. Dark and McFadden (11) employed HPLC and liquid chromatographymass spectrometry for the characterization of coal liquefaction products; and, Clark et al (12) have used both solvent extraction and chromatographic techniques for the isolation of alkanes and PAHs from shale oil. However, none of these methods was developed for the accurate quantitative analysis of individual compounds.

To enhance the accuracy of environmental measurements, we have developed methods for quantitating individual toxic and/or carcinogenic compounds in alternate fuels. In particular, methods for determining the concentrations of several phenols, N-heteroaromatic compounds (aza-arenes) and PAH in shale oil are reported in this paper. Initial emphasis has focused on the evaluation of an acid-base extraction scheme and a preparative HPLC procedure as independent methods for shale oil fractionation. Various gas chromatographic (GC), gas chromatographic-mass spectrometric (GC-MS), and high performance liquid chromatographic methods have been investigated as means of individual compound identification and quantitation.

## Experimental

Shale Oil Sample. The shale oil analyzed in this work is from a 150-ton retort for in-situ simulated combustion operated by the Laramie Energy Research Center, Laramie, Wyoming. The shale is from the Mahogany zone of the Colorado Green River formation. An 8 L sample of this shale oil was obtained by NBS from Bruce R. Clark at Oak Ridge National Laboratory, Oak Ridge, Tennessee. The shale oil underwent centrifugation at Oak Ridge to separate water (∿40%) and sludge from the oil. This shale oil has been utilized for analytical methods development at Oak Ridge (13). A subsample of 1 liter was removed from the 8 liter bulk sample. Aliquots of ∿5 mL each were sealed in amber glass ampoules for subsequent analyses. The samples were analyzed to measure the concentration (μg/g) of pyrene, fluoranthene, benzo(a)-pyrene, benzo(e)pyrene, phenol, o-cresol, 2,4,6-trimethylpyridine, and acridine.

## Extraction

Acid-base extraction. The shale oil sample was separated into three fractions (acids, bases, and neutrals) using an extraction procedure adapted from Schmeltz (14). This procedure is shown schematically in Figure 1 for a 0.5g sample. For the determination of the PAHs an additional liquid-liquid partition step using dimethylformamide (DMF)/water was utilized to separate the aliphatic hydrocarbons from the PAHs. This procedure for the isolation of PAHs in complex mixtures has been previously reported by Bjorseth (15).

HPLC extraction (fractionation). The shale oil sample was diluted (∿0.1g/mL in methylene chloride) prior to fractionation on a preparative scale aminosilane column (μBondapak $NH_2$, 30 cm x 8 mm i.d.). A sample containing approximately 14 mg of shale oil was injected onto the column using a loop injector. A mobile phase flow rate of approximately 5 mL/min was employed.

Standards of the compounds to be determined and the compounds utilized as internal standards for quantitation were injected to determine the appropriate elution volumes for fraction collection. The fractions were collected in centrifuge tubes and reduced to 50-500 μL by passing nitrogen over the sample. Chromatographic conditions for the HPLC fractionations are presented in Tables I, II, and III.

### Quantitation

*HPLC Quantitation*. Analytical liquid chromatographic analyses were performed on an instrument equipped with a gradient pumping system, loop injector and spectrophotometric and spectrofluorimetric detectors. A digital integrator and strip chart recorder were used for data acquisition.

A determination of the volume of the sample loops for both the fractionation and analytical HPLC system was accomplished through use of a gravimetric procedure. The loops were initially filled with mercury. The mercury was swept from the loops into a tared weighing dish with approximately 1 mL of pentane. The bulk of the pentane was decanted and the remainder was allowed to evaporate. This process was repeated five times for each loop. The mass of mercury displaced from the loop was determined gravimetrically. The volumes of the loops were calculated using the density of mercury and were 137.7±1.2 and 12.98±.06 μL, respectively.

As shown in Table I, one of the methods for quantifying phenol and o-cresol was a sequential HPLC procedure. Phenol and *o*-cresol were separated from the shale oil matrix and collected in separate fractions. The concentration of each of these compounds in the collected fractions was determined by use of an internal standard method. A known amount of phenol (as an internal standard) was added to the fraction containing o-cresol and o-cresol was added as an internal standard to the fraction containing phenol. Both fractions were reduced in volume to approximately 100 μL with a stream of nitrogen. These fractions were then chromatographed on an octadecylsilane ($C_{18}$) column using 40% acetonitrile in water as the mobile phase, and ultraviolet detection at 270 nm. The concentration of phenol and o-cresol in the shale oil was then calculated by comparing the chromatographic peak heights of the analyte and internal standards and applying factors for the differences in detector response and losses during evaporation.

Pyrene, fluoranthene and benzo(a)pyrene were also determined by a sequential HPLC method (See Table 1). The PAHs were initially separated from the shale oil matrix and then the analytes were separated from other PAHs by chromatography on a $C_{18}$ column with a water-acetonitrile mobile phase. Further selectivity was obtained by monitoring the chromatographic effluent fluorometrically, with excitation and emission wavelengths optimized for detection of each analyte. Quantitation was achieved using an external standard.

GC Quantitation. Gas chromatographic analyses were performed on a gas chromatograph modified for use with wall-coated open tubular glass capillary columns (WCOT). The resolving power of these columns is illustrated in Figure 2 which is a chromatogram of shale oil bases. It would have been impossible to quantitate these complex mixtures using gas chromatographic methods without these high efficiency columns.

Quantitation by GC was always performed using an internal standard method with peak areas determined using a digital integrator. Internal standard compounds were chosen which possessed similar chemical properties to that of the analyte and were never obscured by measurable chromatographic interferences (co-eluting compounds). The internal standards were added to the shale oil at the earliest possible point in the analysis scheme. Standards containing accurately known amounts of standard and analyte were taken through the entire quantitation procedure to determine response factors. These response factors thereby reflect not only differences in detector response but also chemical and physical properties such as extraction efficiencies and volatility losses which might occur during extract concentration. Details concerning the sample preparation and GC conditions used in the determination of the selected shale oil constituents are summarized in Table II.

GC/MS quantitation. Gas chromatographic-mass spectrometric analyses were performed on a standard gas chromatograph, modified for use with WCOT columns, interfaced to a quadropole mass spectrometer with dual disk data system. Chromatographic columns were interfaced to the mass spectrometer either through a gold jet molecular separator, or an 'open split' (16) constructed of Ni tubing (1/16" OD x 0.010" ID) which was deactivated (17) and restricted to allow a flow rate of 1.5 mL/min into the ion source. The operating pressure in the ion source manifold was $1.0 \times 10^{-5}$ torr. The mass spectrometer was operated in the electron impact mode under the following conditions: interface temperature 250-275°C, ion source 200°C, analyzer 100°C, electron energy 70 eV. Gas chromatographic separations were carried out on the columns and under the conditions noted in Table III.

A standard addition technique was generally used for individual species quantitation (see Table III). For each compound to be determined, four shale oil samples, with different known amounts of the analyte added, were fractionated. The standard additions were made over a range of zero to three times the approximate concentration of the analyte, based on a preliminary quantitative determination of the compound in the shale oil using an external standard method. The 'spiked' shale oil samples were subjected to either an acid/base solvent extraction or an HPLC fractionation. The samples were reduced to 100 µL under a stream of nitrogen, and suitable aliquots analyzed by GC/MS with selected ion monitoring. To circumvent the need for accurately measuring volumes during the extraction or fractionation, and to compensate for variable injection volumes onto the GC column, a second compound natively present in the shale oil, and in the same compound class as the compound being determined, was monitored as a volume correction standard. The specific compounds used as volume correction standards for each analyte are listed in Table III. Selected ion monitoring was chosen as the means of analysis for its sensitivity and selectivity. The ions (generally the molecular ions) for the analytes and the internal standards (volume correction standards) were monitored in real time in 0.1 amu increments to insure that the signal was sampled at the top of the mass peak. Dwell times of either 50 or 100 ms were used to insure at least 20 data points across a chromatographic peak. Single ion records were integrated after each run, and a ratio of the peak area for the analyte to the peak area of the internal standard (volume correction standard) was computed. This ratio was plotted against the concentration of the analyte (in ppm) added to the shale oil. The concentration of the analyte natively present in the shale oil was determined from the intercept with the abscissa, using a linear least squares program.

Fluoranthene and pyrene were also determined in the shale oil without any prior acid/base extraction or HPLC fractionation. Approximately 0.5g of shale oil was diluted to 10 mL with methylene chloride. A known amount of 9,10-dimethylanthracene (∿50 μg) was added to the solution as an internal standard. One to two μL aliquots of this solution were analyzed by GC/MS using selected ion monitoring. The chromatographic conditions were as noted in Table III. Single ion records for the $^m/z$ 202 ion (for fluoranthene and pyrene) and the $^m/z$ 206 ion (for 9,10-dimethylanthracene) were clean enough to allow integration of peak areas Response factors for fluoranthene and pyrene relative to the

9,10-dimethylanthracene were determined under identical GC/MS conditions from gravimetrically prepared solutions of these compounds. Concentrations of fluoranthene and pyrene were determined from these response factors and ratios of the area of the compound being determined to that of the internal standard.

## Results and Discussion

The major aim of this study was to develop independent analytical methods for the quantitative determination of individual toxic and/or carcinogenic compounds in an alternate fuel. The development of a minimum of two such independent methods is a necessary prerequisite to the certification of a Standard Reference Material needed as a quality assurance standard in the rapidly expanding fields of energy, environmental and trace organic analytical research. We have shown that individual organic compounds can be quantitated in a shale oil matrix and that diverse methodology will, if properly applied, yield comparable results. In addition we have reported a new HPLC method for preliminary shale oil fractionation, a novel GC/MS quantitation technique which has been shown to greatly enhance analytical selectivity relative to conventional GC techniques, and finally an HPLC fluorescence method which allows individual PAHs to be measured in the presence of other PAHs. The success of the HPLC fluorescence method can be attributed to: 1) the chromatographic selectivity obtained by reverse phase HPLC, and 2) the detection selectivity obtained through use of fluorometric monitoring of the chromatographic effluent. (PAHs have very characteristic excitation and emission spectroscopic properties which can be used both for identification and selective detection.) The results obtained by the two independent methods of sample extraction (classical acid/base solvent extraction and HPLC fractionation) and three methods of quantitation (high performance liquid chromatography, gas chromatography with flame ionization detection and gas chromatography-mass spectrometry using single ion monitoring) are summarized in Table IV.

Many laboratories are now involved in qualitative examinations of pilot run alternate fuels, and an increasing number of laboratories are becoming involved in the quantitative analysis of constituents of alternate fuels. However, the accuracy base needed to compare quantitative analyses performed by different investigators is not now available. As part of a preliminary assessment of the environmental impact of oil shale development, researchers at the TRW Environmental Engineering Division and the Denver Research Institute summarized the available quantitative data on the presence of benzo(a)pyrene in various fuels and natural materials (18). In addition several researchers have determined the concentrations of various PAHs in a limited number of coal-derived liquefaction products (19,20). However, even in these limited studies the basis for intercomparison of data is lacking.

In simultaneously developing independent analytical methods as presented in this paper, one is afforded a unique opportunity for comparative evaluation of efficiency and precision of the methods. The greatest improvement in efficiency noted during this study was the incorporation of HPLC fractionation as a replacement for classical extraction techniques. The acid/base extraction (Fig. 1) is a laborious procedure which requires several days to generate the acidic, basic and neutral fractions. Furthermore, once the extraction has been completed, the samples must be subjected to a high resolution chromatographic separation to allow individual components to be sufficiently separated for quantitation free from interferences. On the other hand, the HPLC fractionation procedure provides a rapid (less than 1 h) method of preparing shale oil fractions which are considerably less complex than the three initial fractions generated by the acid/base extraction scheme. Using a preparative scale aminosilane column and modifying the mobile phase composition from 100 percent hexane to 100 percent methylene chloride, it is possible to elute a wide range of compounds from non-polar PAHs to the more polar phenols and aza-arenes. Figure 3 is an ultraviolet detection recording at 270 nm of the liquid chromatography to generate the phenolic fractions. The upper trace is a chromatogram of shale oil and the lower trace is a chromatogram of various compounds used to determine retention volumes for the phenols of interest. As one can see the PAHs are eluted unretained when using 100 percent methylene chloride as the mobile phase. (The PAHs are isolated according to the number of condensed rings using n-hexane as the mobile phase [21]). One should also note in comparing results obtained on the small polar compounds, phenol, o-cresol, and 2,4,6-trimethylpyridine, that there is an indication of greater precision in any single method of quantitation when using HPLC fractionation rather than the acid/base extraction.

As mentioned above, in addition to the two methods of sample preparation, three methods of individual compound quantitation were utilized. The gas and liquid chromatographic methods of quantitation, which utilized either internal or external standards, required some assumptions and/or prior analyses. For the internal standard methods one had to assume that the standard behaved similarly to the component of interest and one had to show that its native level in the sample was insignificant relative to the amount added (which should be added to approximate the concentration of the analyte). When all appropriate internal standards were natively present at a significant concentration (the phenols in this study), the internal standard had to be added after HPLC fractionation had segregated the analyte, thereby requiring the assumption that no losses ocurred during fractionation. Where only an external standard was used an assumption of instrument (detector) stability was required, as well as an assumption that no losses occurred during sample preparation. The gas chromatography-mass spectrometry with single ion monitoring and standard addition techniques required none of these assumptions and provided further selectivity by lack of interference from co-eluting compounds in the gas chromatography due to the mass selectivity. To the extent that values generated by GC-MS with standard addition agreed with the HPLC and GC only values, the assumptions discussed above were valid.

The use of GC/MS single ion monitoring in conjunction with standard addition techniques provides a novel, accurate and extremely selective means for individual compound quantitation. The only possible interference in this mode of operation is a co-eluting compound with a peak at the same m/z ratio in its mass spectrum. To minimize this possibility, several other ions in the spectrum of the component of interest are periodically monitored to assure that the relative peak areas for these ions are in the same ratio as for an authentic sample of the pure analyte.

To assure maximum sensitivity the ion to be used for quantitation was monitored at several 0.1 amu intervals to confirm that the signal of maximum intensity was used for peak area calculations. This principle is demonstrated in Figure 4 which contains single ion records for 2,4,6-trimethylpyridine ($M^+$, m/z 121) and for a dimethylethylpyridine [$(M-1)^+$, m/z 134], the volume correction standard. Three independent area determinations were made at each peak maximum (m/z 121.2 and m/z 134.2). These numbers were averaged and the area ratio was then used for one data point in the standard addition determination (see Figure 5). Despite the mass specificity, a small shoulder which represented about 2% of the total peak area was observed on the m/z 134 peak. As can be seen in Figure 5, several GC-MS determinations were made at each concentration of added 2,4,6-trimethylpyridine and the x-intercept of the least squares fit of the data indicated a native concentration of 1214±64 ppm 2,4,6-trimethylpyridine in the shale oil sample.

As can be seen from Table IV the overall agreement between the various methods of quantitation and extraction was quite good, even at the 95% confidence level. The poorest between-method precision was obtained in the determination of 2,4,6-trimethylpyridine. This imprecision was probably related to the sample preparation aspects of the work, due to the volatility of the compound. An indication of this is the fact that the GC-MS standard addition value is the highest and should be independent of volatility losses.

This shale oil sample has been analyzed by various national and university laboratories, to evaluate interlaboratory precision in the determination of trace organic compounds in alternate fuels. The results of this intercomparison study are being compiled for publication.

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In order to specify procedures adequately, it has been necessary to identify some commercial materials in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

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Table I. HPLC Methods for the Analysis of Shale Oil

| Compound Determined | Sample Preparation | Internal or External Standard | Chromatographic Conditions for Analysis |
|---|---|---|---|
| Pyrene<br>Fluoranthene | HPLC fractionation - 2% $CH_2Cl_2$ in hexane, collect pyrene/fluoranthene fraction. | External standards of pyrene and fluoranthene to determine fluorescence response. | Reverse phase C-18 column, 70/30% $CH_3CN/H_2O$, Fluorescence detection: pyrene (excitation - 337 nm, emission - 370 nm), fluoranthene (excitation - 295 nm, emission - 463 nm). |
| Benzo(a)pyrene | HPLC fractionation - 2% $CH_2Cl_2$ in hexane, collect benzo(a)-pyrene fraction. | External standard of benzo(a)pyrene. | Reverse phase C-18 column, 40-100% linear gradient $CH_3CN$ in $H_2O$ in 30 min., Fluorescence detection: benzo(a)pyrene (excitation 295 nm, emission - 403 nm). |
| Phenol | HPLC fractionation - $CH_2Cl_2$ as mobile phase - baseline resolution of o-cresol, p-cresol, and phenol standards, collect phenol fraction only. | o-Cresol added after fractionation. | Reverse phase C-18 column, 40/60% $CH_3CN/H_2O$, UV absorption detection at 270 nm. |
| o-Cresol | HPLC fractionation - $CH_2Cl_2$ as mobile phase, collect o-cresol fraction only. | Phenol added after fractionation. | Reverse phase C-18 column, 40/60% $CH_3CN/H_2O$, UV absorption detection at 270 nm. |
| Acridine | HPLC fractionation - 10% $CH_2Cl_2$ in hexane, collect acridine fraction. | External standard of acridine to determine UV response. | Reverse phase C-18 column, 0-50% linear gradient $CH_3CN$ in $H_2O$ in 20 min.<br>UV absorption detection at 254 nm. |

Table II. GC Methods for the Analysis of Shale Oil

| Compound Determined | Sample Preparation | Internal Standard | Chromatographic Column | Operating Conditions |
|---|---|---|---|---|
| Pyrene<br>Fluoranthene | HPLC fractionation - 2% $CH_2Cl_2$ in hexane, pyrene/fluoranthene fraction collected. | 3-methylpyrene added prior to fractionation. | Carbowax 20 M WCOT, 30 m x 0.30 mm i.d. | $T_c^*$ = 220 °C, $T_i$ = 300 °C, $T_d$ = 300 °C |
| Pyrene<br>Fluoranthene | Acid/base extraction - neutral fraction isolated, DMF partition to isolate PAHs | 9,10-dimethylanthracene added prior to extraction | SE-52 WCOT, 30 m x 0.25 mm i.d. | $T_c$ = 190 °C, $T_i$ = 300 °C, $T_d$ = 300 °C |
| Phenol | HPLC fractionation - $CH_2Cl_2$ as mobile phase, collect phenol fraction only (baseline resolution of o-cresol, p-cresol, and phenol standards). | p-cresol added after fractionation. | SP 1000 WCOT, 30 m x 0.25 mm i.d. | $T_c$ = 180 °C, $T_i$ = 300 °C, $T_d$ = 300 °C |
| o-Cresol | HPLC fractionation - $CH_2Cl_2$ as mobile phase, collect o-cresol fraction only. | p-cresol added after fractionation. | Carbowax 20 M WCOT, 30 m x 0.30 mm i.d. | $T_c$ = 150 °C, $T_i$ = 250 °C, $T_d$ = 250 °C |
| 2,4,6-trimethylpyridine | HPLC fractionation - $CH_2Cl_2$ as mobile phase, collect 2,4,6,-trimethylpyridine fraction. | 4-ethylpyridine added after fractionation. | SP 1000 WCOT, 30 m x 0.25 mm i.d. | $T_c$ = 100 °C, $T_i$ = 200 °C, $T_d$ = 250 ° |
| 2,4,6-trimethylpyridine | Acid/base extraction - base fraction isolated. | 4-ethylpyridine added prior to extraction. | SP 1000 WCOT, 30 m x 0.25 mm i.d. | $T_c$ = 100 °C, $T_i$ = 350 °C, $T_d$ = 350 °C |

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*$T_c$ = Column temperature

$T_i$ = Injector temperature

Table III. GC/MS Methods for the Analysis of Shale Oil

| Compound Determined | Sample Preparation | Internal Standard (Volume Correction) | Ions Monitored | Chromatographic Column | Operating Conditions | GC/MS Interface |
|---|---|---|---|---|---|---|
| Pyrene<br>Fluoranthene | HPLC fractionation-2% $CH_2Cl_2$ in hexane collect anthracene through fluoranthene fraction. | phenanthrene + anthracene for volume correction | 202<br>178 | SE-30 WCOT 30m x 0.50mm i.d. | 150°C for 8 min, 220°C at 2°C /min. | single stage gold jet |
| Pyrene<br>Fluoranthene | 0.05g shale oil/mL $CH_2Cl_2$ solution - direct inection | 9,10-dimethylanthracene added | 202<br>206 | SE-52 WCOT 30m x 0.25mm i.d. | 200°C for 2 min, 260°C at 2°C/min. | Ni, open split |
| Benzo(a)pyrene<br>Benzo(e)pyrene | HPLC fractionation-3.5% $CH_2Cl_2$ in hexane collect fraction containing benzo(o) pyrene, benzo(e) pyrene, and perylene | perylene added prior to fractionation | 252 | SE-52 WCOT 30m x 0.25mm i.d. | 200°C for 2 min, 260°C at 2°C/min. | Ni, open split |
| Benzo(a)pyrene<br>Benzo(e)pyrene | Acid/base extraction - DMF partition of neutral fraction | perylene added prior to extraction | 252 | SE-52 WCOT 30m x 0.25mm i.d. | 200°C for 2 min, 260°C at 2°C/min. | Ni, open split |
| Phenol<br>o-Cresol | (1) HPLC fractionation - $CH_2Cl_2$ as mobile phase, collect o-cresol through phenol fraction<br>(2) Acid/base extraction-isolate acid fraction. | m- + p-cresol for volume correction | 94<br>108 | 0.1%SP-1000 on 80/100 Carbopak C | 170°C isothermal | single stage gold jet |
| 2,4,6-Trimethylpyridine | HPLC fractionation-$CH_2Cl_2$ as mobile phase, collect quinoline through 2,4,6-trimethylpyridine fraction | a dimethylethylpyridine isomer for volume correaction | 121<br>134 | SP-2100 WCOT, 30m x 0.25mm i.d. | 90°C for 4 min, 200°C at 2°C/min | Ni, open split |

Table III. GC/MS Methods for the Analysis of Shale Oil

| Compound Determined | Sample Preparation | Internal Standard (Volume Correction) | Ions Monitored | Chromatographic Column | Operating Conditions | GC/MS Interface |
|---|---|---|---|---|---|---|
| Acridine | HPLC fractionation-10% $CH_2Cl_2$ in hexane, collect acridine fraction | benzoquinoline for volume correction | 179 | SE-52 WCOT, 17m x 0.25mm i.d. | 160°C for 2 min, 250°C at 2°/min | Ni, open split |

## Table IV. Shale Oil Analysis
(ppm, 95% confidence level)

| Compound | HPLC Extraction Quantitation by | | | Acid/Base Extraction Quantitation by | | No Extraction Quantitation by |
|---|---|---|---|---|---|---|
| | LC | GC | GC/MS | GC | GC/MS | GC/MS |
| Pyrene | 108 ± 16 | 101 ± 4 | 102 ± 9 | 94 ± 10 | - | 104 ± 8 |
| Fluoranthene | 53 ± 6 | 55 ± 6 | 62 ± 5 | 75 ± 5 | - | 58 ± 5 |
| Benzo(a)pyrene | 21 ± 3 | - | 21 ± 5 | - | 24 ± 2 | - |
| Benzo(e)pyrene | - | - | 20 ± 6 | - | 22 ± 5 | - |
| Phenol | 383 ± 50 | 387 ± 26 | 416 ± 28 | - | 334 ± 63 | - |
| o-Cresol | 330 ± 34 | 334 ± 86 | 350 ± 16 | - | 322 ± 45 | - |
| 2,4,6-trimethyl-pyridine | - | 912 ± 26 | 1214 ± 64 | 988 ± 56 | - | - |
| Acridine | 6.0 ± 2.4 | - | 4.4 ± 0.3 | - | - | - |

# Figure Captions

1 Solvent extraction scheme for the preparation of shale oil sample, adapted from Schmeltz (14).

2 Capillary gas chromatogram of shale oil bases. Conditions: 30m SP-1000 column, 100 °C for 4 min and then temperature programmed to 220 °C at 2°/min, flame ionization detection.

3 Preparative scale liquid chromatogram of shale oil. The upper trace is a chromatogram of shale oil and the lower trace is a chromatogram of a mixture of pure compounds used to determine retention volumes of phenolic compounds. (2,4,6-trimeϕOH ≡ 2,4,6-trimethylphenol). Conditions: semi-preparative aminosilane column, methylene chloride mobile phase and ultraviolet detection at 254 nm.

4 Single ion records for 2,4,6-trimethylpyridine (TMP) and a dimethylethylpyridine (DMEP). Three area determinations for each peak are shown at the m/z value of maximum intensity. The area of a small shoulder on the DMEP peak is also indicated.

5 Linear least squares fit for the data point obtained in the determination of 2,4,6-trimethylpyridine (2,4,6-TMP) by the standard addition method. The absolute value of the x-intercept represents the negative of the concentration of the analyte in the sample.

### e. Existing NBS-SRM's Useful in Characterizing Oil Shale and Oil Shale Products

Over eighty SRM's are now being used to assure measurement compatibility in air and water pollution analyses. Some of these materials could be useful and provide a common reference base for those measurements being made in on-going oil shale projects. Those materials currently available from NBS which could be useful in trace element measurements in oil shale and oil shale products are given in Table 4-2. It should be noted that several standards are available for the same element, but indicated in the table by different numbers (e.g. SRM 1621 and 1622). This occurs because the same element has been certified at varying concentrations in the same matrix. Additional information on the materials listed in the above Table can be found in Appendix B.

## TABLE 4-2

### Existing NBS-SRM's Applicable to Characterization of Oil Shale/Oil Shale Products

(Liquids)

| SRM Number | Type |
|---|---|
| 1621 | Sulfur in Residual Fuel Oil |
| 1622 | Sulfur in Residual Fuel Oil |
| 1623 | Sulfur in Residual Fuel Oil |
| 1624 | Sulfur in Distillate Fuel Oil |
| 1634 | Trace Elements in Residual Oil |
| 1636 | Lead in Reference Fuel |
| 1637 | Lead in Reference Fuel |
| 1638 | Lead in Reference Fuel |

(Solids)

| | |
|---|---|
| 1630 | Mercury in Coal |
| 1631a | Sulfur in Coal |
| 1632a | Trace Elements in Bituminous Coal |
| 1633a | Trace Elements in Coal Fly Ash |
| 1635 | Trace Elements in Sub-bituminous Coal |
| 1648 | Trace Elements in Urban Particulate Matter |

## SECTION 5

## RECOMMENDATIONS FOR FUTURE OIL SHALE PROJECTS

The environmental impact associated with commercial oil shale operations can be expected to produce air and water pollutants, in addition to other potential adverse impacts on the environment. Development of measurement methods and/or standards to ensure quality baseline data and effective monitoring systems is a necessity if logical and rational policy decisions are to prevail in developing mitigation strategies for adverse environmental impacts caused by the oil shale industry.

All commercial shale operations will be required to preserve water resources and control effluent discharges. To meet these requirements, effluents will need to be characterized, controlled, and monitored. Similarly, process and fugitive emission into the ambient air may arise from a variety of sources related to oil shale processing and a monitoring program for these emissions will also be required. Thus, appropriate standards must be available to provide data quality assurance for measurements made on oil shale effluents as well as emissions into the atmosphere. More importantly, accurate measurement methods must be in place to identify, quantify and certify individual pollutants in a variety of complex matrices which will serve as standards/SRM's for the oil shale industry.

Recommendations for further work at NBS in oil shale products is summarized in Table 5-1. These recommendations reflect suggestions/input obtained during conversations with scientists involved with the characterization of oil shale products.

## Table 5-1

## Recommendations for Further NBS Work

- Produce a Raw Oil Shale SRM, certified for all trace elements of potential environmental or product development concern
- Develop methods needed to produce a Raw Oil Shale SRM, certified for trace organic pollutants (with focus on criteria organic pollutants)
- Develop/modify methodologies necessary to certify all trace elements of potential environmental or product development concern in: 1) Shale Oil; 2) Oil Shale retort water; 3) and/or other associated aqueous phases
- Extend the trace organic certification program on shale oil to include more criteria pollutants (specifics to be determined through negotiations with interested parties)
- Assist responsible monitoring agencies in developing protocols for "traceability" in oil shale (and associated products) measurements

# APPENDIX A

## Manuscripts Prepared for/Presented During Workshop

# PREPARATION OF STANDARD OIL-SHALE SAMPLES

## OS-1, SS-1, and SS-2

Thomas Wildeman
Chemistry Department
Colorado School of Mines
Golden, Colorado 80401

Work performed under a grant from the Colorado Energy Research Institute

This report provides background on the standard oil shale sample, OS-1, and the two standard spent shale samples, SS-1 and SS-2. It describes the geology of the site, the mining and retorting processes used, the manner of preparation of the samples, possible sources of contamination, and suggestions on further preparation of standard samples. References to more detailed discussion are also included.

## Site Description, Geology, and Chemistry

The shale samples came from the Dow mine of Colony Development Co., so named because it was purchased from the Dow Chemical Co.. The Colony Development Oper. is a consortium of energy corporations with The Oil Shale Corp. (TOSCO) and the Atlantic Richfield Co. (ARCO) being the primary participants (1, 2). The location of the Dow Property (shown in Figure 1) is at the head of Parachute Creek in the Piceance Creek Basin, Colorado, 17 miles north of Grand Valley, Colorado (1).

The actual mining operation is on two 30 foot vertical sections called the Upper Bench and Lower Bench which start at 10 feet below the Mahogany Marker and proceed down for 60 feet. This places the samples in the Mahogany Zone of the Parachute Creek Member of the Green River Formation as shown in figure 2 (3, 4). Oil-shale reserve experts call this the Mahogany Zone of the Upper Oil-Shale zone and consider it to be one of the richest oil zones in the Piceance Creek Basin with yields ranging from 28 to 79 gallons/ton (4). Assays conducted by TOSCO show the Upper Bench shale as yielding 37-39 gal/ton and the Lower Bench shale 33 gal/ton.

Roehler (3) describes the depositional environment as saline

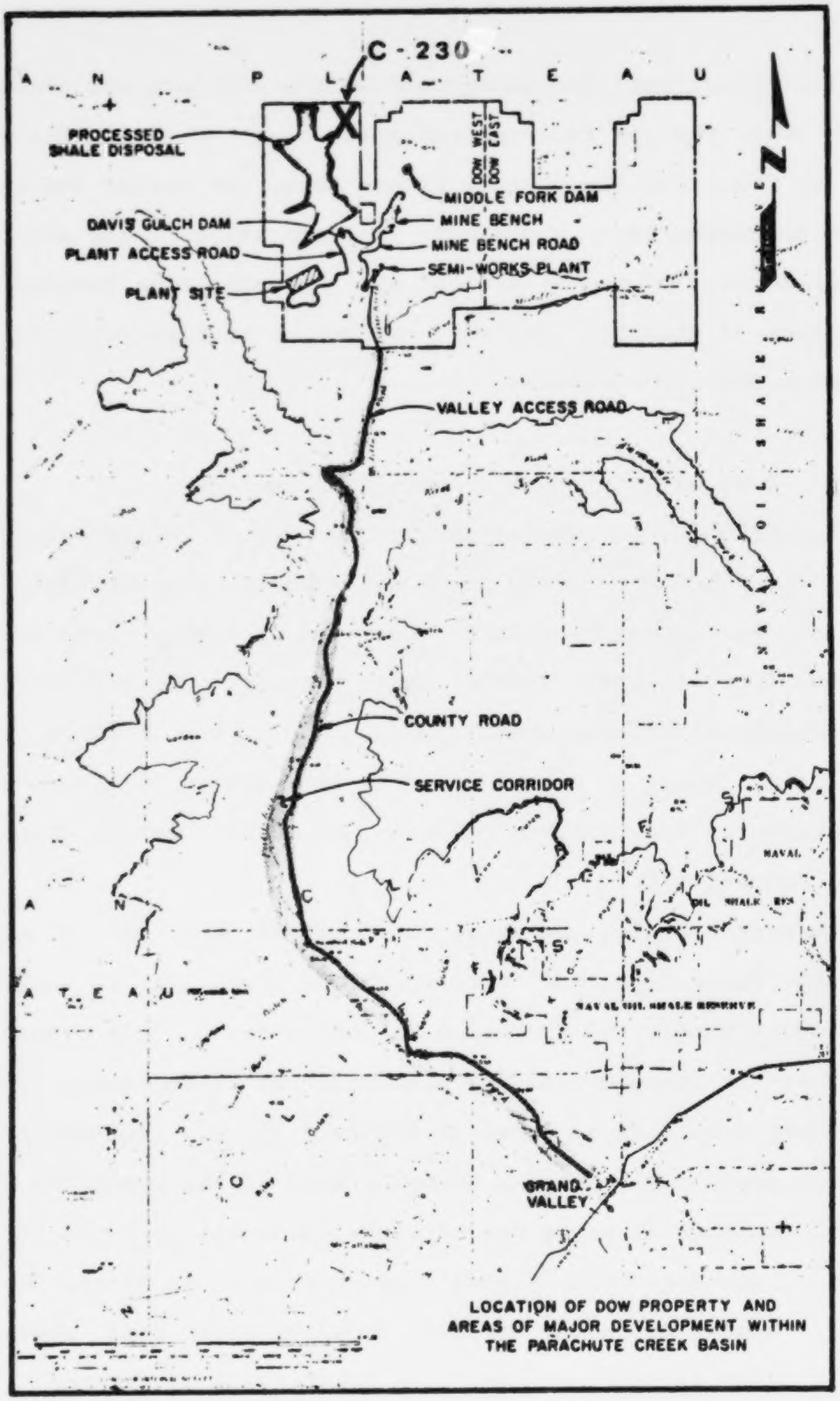
C - 230
A N P L A T E A U
PROCESSED SHALE DISPOSAL
DAVIS GULCH DAM
PLANT ACCESS ROAD
PLANT SITE
DOW WEST
DOW EAST
MIDDLE FORK DAM
MINE BENCH
MINE BENCH ROAD
SEMI-WORKS PLANT
N
NAVAL OIL SHALE RESERVE
VALLEY ACCESS ROAD
COUNTY ROAD
SERVICE CORRIDOR
NAVAL OIL SHALE RESERVE
GRAND VALLEY
LOCATION OF DOW PROPERTY AND AREAS OF MAJOR DEVELOPMENT WITHIN THE PARACHUTE CREEK BASIN

Figure 1. Taken from Reference (1).

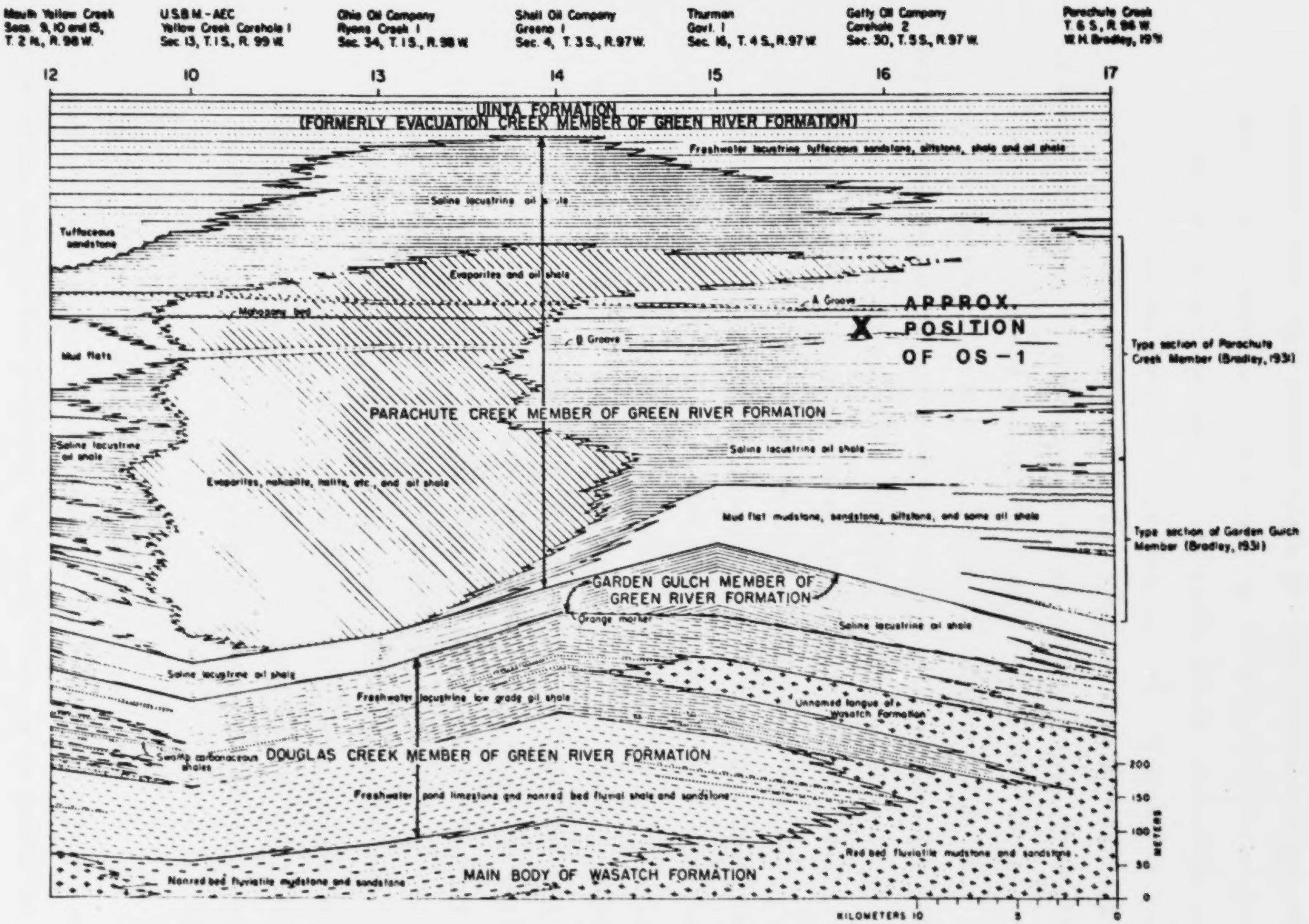
Mouth Yellow Creek
Secs. 9, 10 and 15, T. 2 N., R. 98 W.
U.S.B.M.-AEC
Yellow Creek Corehole 1
Sec 13, T. 1 S., R. 99 W.
Ohio Oil Company
Ryans Creek 1
Sec. 34, T. 1 S., R. 98 W.
Shell Oil Company
Greeno 1
Sec. 4, T. 3 S., R. 97 W.
Thurman
Govt. 1
Sec. 16, T. 4 S., R. 97 W.
Getty Oil Company
Corehole 2
Sec. 30, T. 5 S., R. 97 W.
Parachute Creek
T. 6 S., R. 96 W.
W. H. Bradley, 1931
12
10
13
14
15
16
17
UINTA FORMATION
(FORMERLY EVACUATION CREEK MEMBER OF GREEN RIVER FORMATION)
Freshwater lacustrine tuffaceous sandstone, siltstone, shale and oil shale
Saline lacustrine oil shale
Tuffaceous sandstone
Evaporites and oil shale
A Groove
APPROX.
X POSITION
OF OS-1
Mahogany bed
B Groove
Mud flats
Type section of Parachute Creek Member (Bradley, 1931)
PARACHUTE CREEK MEMBER OF GREEN RIVER FORMATION
Saline lacustrine oil shale
Saline lacustrine oil shale
Evaporites, nahcolite, halite, etc., and oil shale
Mud flat mudstone, sandstone, siltstone, and some oil shale
Type section of Garden Gulch Member (Bradley, 1931)
GARDEN GULCH MEMBER OF GREEN RIVER FORMATION
Orange marker
Saline lacustrine oil shale
Saline lacustrine oil shale
Freshwater lacustrine low grade oil shale
Unnamed tongue of Wasatch Formation
Swamp carbonaceous shales
DOUGLAS CREEK MEMBER OF GREEN RIVER FORMATION
Freshwater pond limestone and nonred bed fluvial shale and sandstone
Red bed fluviatile mudstone and sandstone
Nonred bed fluviatile mudstone and sandstone
MAIN BODY OF WASATCH FORMATION
200
150
100
50
0
METERS
KILOMETERS 10
5
0

**Figure 2.** Northwest-southeast cross section of Eocene rocks in the Piceance Creek basin showing stratigraphic units and environments of deposition. Taken from Reference 3.

lacustrine (saltwater lake) in which organic muds were deposited and saline waters enhanced the growth of planktonic algae. The brines settled to deeper parts of the lake so that evaporite-deposit minerals are not as prevalent in these shales.

Although there is no published drill core information on the Dow Property, Union Oil Co. has released information on its property which lies to the south and west of the Dow Property (5). The drill core data published in Donnell's report (4) contain no information on this area. Perhaps the most significant study relating to these samples is that by Desborough's group (6, 7) on a sample from a drill core which lies on the Dow Property. The approximate site of this hole labeled C-230 is shown in figure 1. Even though the vertical variation in the Green River Formation can be considerable, the proximity of this sample to the standard oil-shales described here will make for interesting comparisons.

Table I lists the composition information on this sample. The four samples Desborough (6) analyzed from the Mahogany Zone in Colorado are chemically and mineralogically quite similar; however, the range in oil yield was 48 to 71 gal/ton which is higher than the 33-39 gal/ton range of the Dow mine. It appears that shales with lower oil yields have greater concentrations of dolomite and smaller concentrations of quartz and pyrite. Other data available on this C-230 sample include the chemical composition of carbonate grains, electron microprobe images, and information on arsenic (6, 7).

## Mining and Retorting Procedures

The mining and retorting processes to be used on the Dow Property are considered to be the closest to immediate industrical scale-up and

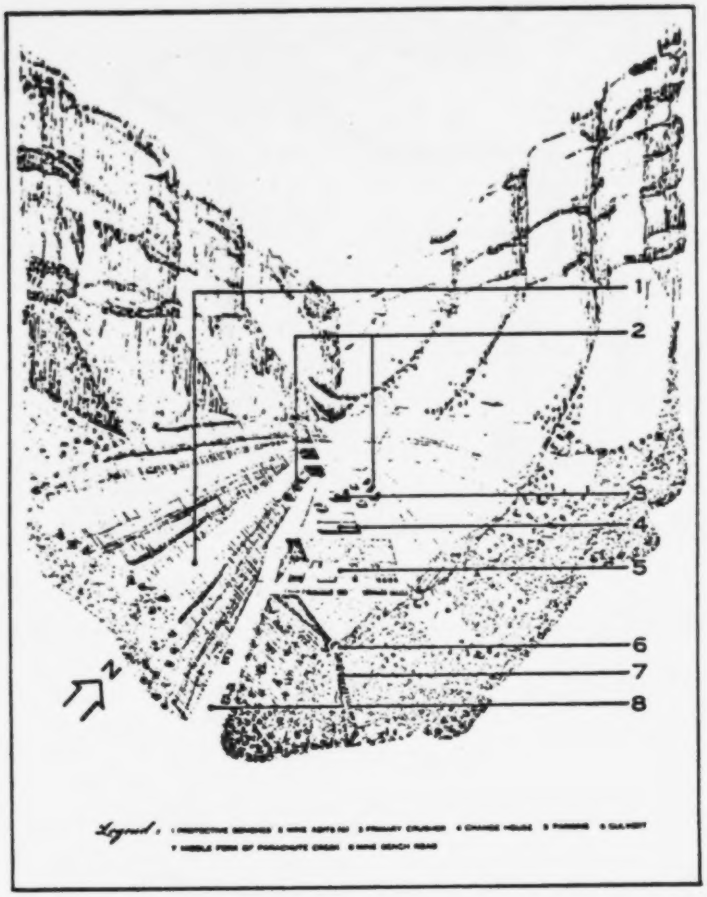
1
2
3
4
5
6
7
8
N
Legend: 1 PROTECTIVE BENCHES 2 MINE ADITS (4) 3 PRIMARY CRUSHER 4 CHANGE HOUSE 5 PARKING 6 CULVERT
7 MIDDLE FORK OF PARACHUTE CREEK 8 MINE BENCH ROAD

Figure 3. Colony mining operation in the Middle Fork Canyon.

Figures taken from Reference 8.

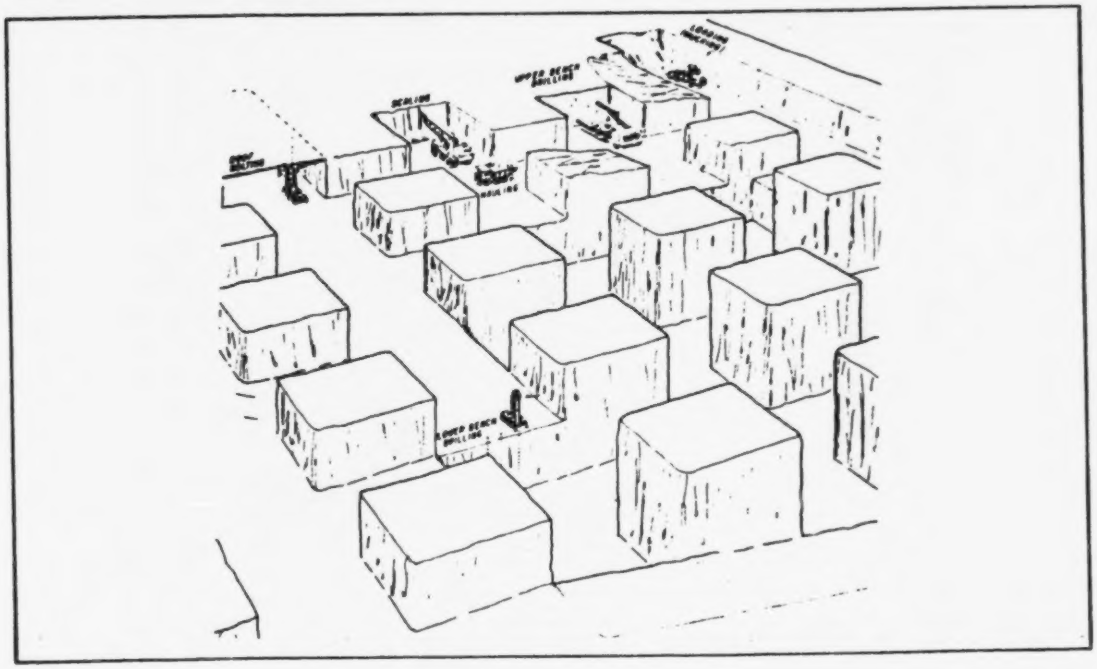
SCALING
UPPER BENCH DRILLING
HAULING
LOWER BENCH DRILLING

Figure 4. Room-and-pillar two bench mining cycle.

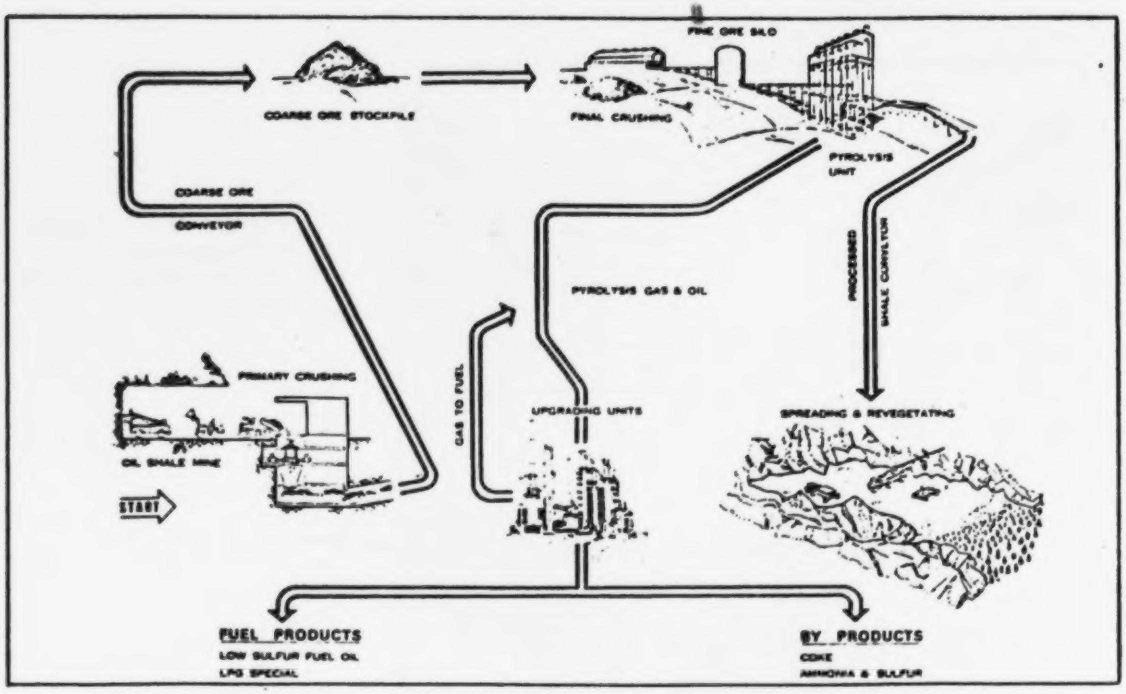
FINE ORE SILO
COARSE ORE STOCKPILE
FINAL CRUSHING
PYROLYSIS UNIT
COARSE ORE CONVEYOR
PYROLYSIS GAS & OIL
PROCESSED SHALE CONVEYOR
PRIMARY CRUSHING
GAS TO FUEL
UPGRADING UNITS
SPREADING & REVEGETATING
OIL SHALE MINE
START
FUEL PRODUCTS
LOW SULFUR FUEL OIL
LPG SPECIAL
BY PRODUCTS
COKE
AMMONIA & SULFUR

Figure 5. A schematic of Colony's mining and oil-shale processing procedure taken from reference 8.

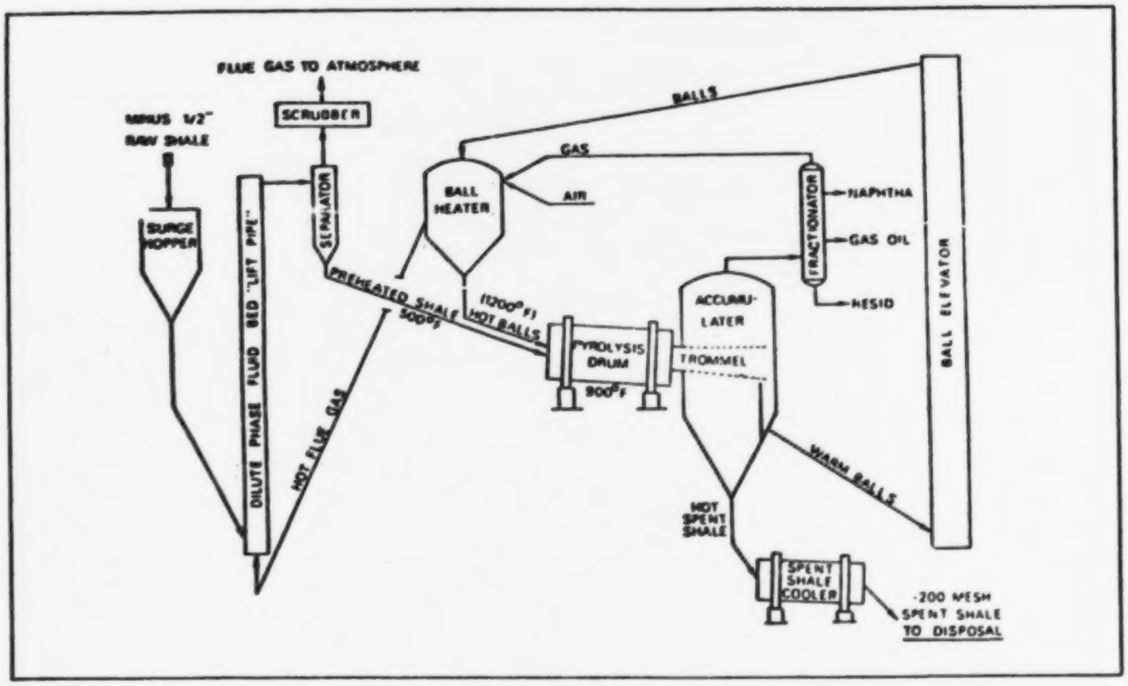
FLUE GAS TO ATMOSPHERE
SCRUBBER
MINUS 1/2" RAW SHALE
SURGE HOPPER
DILUTE PHASE FLUID BED "LIFT PIPE"
SEPARATOR
BALLS
BALL HEATER
GAS
AIR
FRACTIONATOR
NAPHTHA
GAS OIL
RESID
PREHEATED SHALE 500°F
(1200°F) HOT BALLS
PYROLYSIS DRUM
900°F
ACCUMULATER
TROMMEL
BALL ELEVATOR
HOT FLUE GAS
WARM BALLS
HOT SPENT SHALE
SPENT SHALE COOLER
-200 MESH SPENT SHALE TO DISPOSAL

Figure 6. A flow diagram of the TOSCO II process taken from reference 2.

hence have been well studied and described. Figure 3 shows the layout of the mining operation in the canyon of the Middle Fork of Parachute Creek and figure 4 shows the function of the Upper and Lower Benches in the mine (1, 8). If operating today, this would be the largest room-and-pillar mine in the world.

The TOSCO II retorting process has also been described in detail (1, 2, 9). Figure 5 schematically shows the whole process and figure 6 is a flow sheet of the retorting operation. This process has some unique characteristics that should be kept in mind. First, it uses recycled hot solids (½" ceramic balls) as a heating agent as opposed to internal combustion of gases within the retort or external fuel-fired retorting. This allows better control of the retort temperature and the TOSCO II process probably keeps the temperature lower (482°C, 900°F) than other retorting methods. Second, the feed stock is crushed to a smaller size (-½" mesh, including fines) than other processes which exclude feed stock below 1/8" and crush to 3 in. pieces. Furthermore, the pyrolysis drum crushes the shale still further so that the bulk of the spent shale is less than 200 mesh; other processes can end up with clinkers. Finally, the oil recovery in the TOSCO II process appears to be better, typically 100% of Fischer Assay, than other processes, about 80-90% of Fischer assay.

## Preparation of Standard Samples

All the samples were mined from fresh faces in the Dow mine in 1974, crushed to -½ mesh and delivered in 100 ton lots to the TOSCO research facility in Golden, Colorado. OS-1 was taken from a residual pile of approximately 3 tons of -½ mesh feed stock which was mined from the Upper Bench and assayed at 37 gal/ton. SS-2 is spent shale resulting from the retort operations at TOSCO's

Denver pilot plant on Nov. 11, 1974 on the same feed stock from which OS-1 was taken. SS-1 is spent shale resulting from retort operations at the pilot plant on August 23, 1974 on feed stock from the Lower Bench which assayed at 33 gal/ton. The amounts collected were 31 lb. of SS-1, 24 lb. of SS-2, and 60 lb. of OS-1.

The spent shale samples were wet with tap water and so were air dried at room temperature for two weeks. Ninety percent of the spent shale was -200 mesh material the other 10% was partially retorted stock which was greater than 10 mesh. These pieces were hand ground in a porcelain mortar and added to the sample. Approximately 5% of SS-1 and SS-2 will not pass through a 100 mesh sieve. No other processing of the spent shale samples was done prior to blending and splitting.

The raw shale required extensive crushing and grinding to prepare it for blending and splitting. The objective here is to grind to minus 65 mesh since the analysts at TOSCO have shown that this will provide a more representative sample of the bulk feed stock when 100 gm is used for Fischer assay (10). First, the half inch feed stock was crushed in a hardened steel jaw mill to minus 4 mesh particles and then in a hardened steel roller mill to minus 10 mesh particles. Grinding was then attempted using a ceramic ball mill but the shale particles are surprisingly hard and resinous and the ceramic balls just bounced off the particles. Grinding to minus 65 mesh would have taken at least one day for each charge, so this method of grinding was abandoned. Instead a "shatterbox" was used. This was quite effective, but the action of the grinding rings generated some heat. Charges were ground for no more than 30 sec. so the loss of volatiles would be kept to a minimum. The

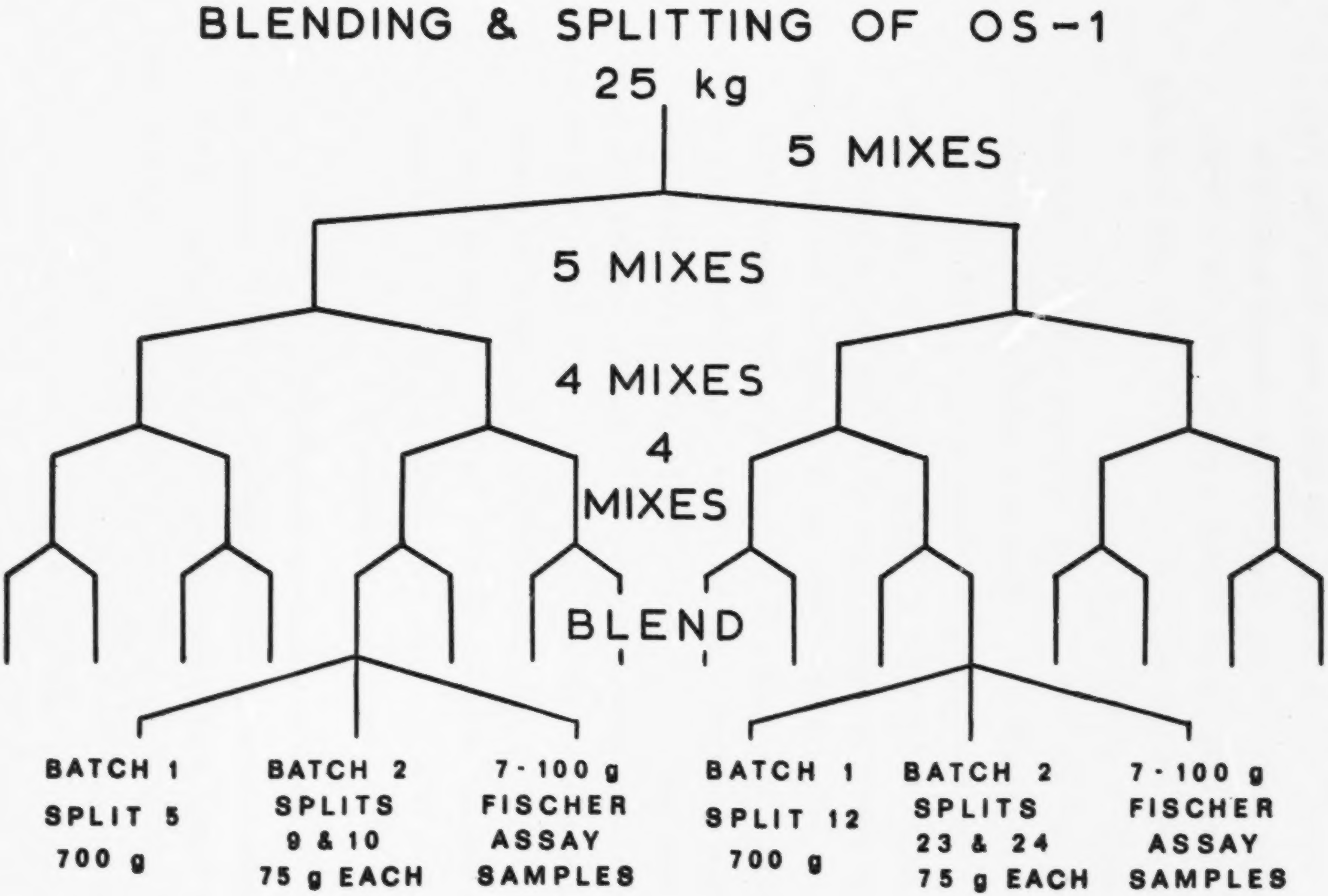
BLENDING & SPLITTING OF OS-1
25 kg
5 MIXES
5 MIXES
4 MIXES
4
MIXES
BLEND
BATCH 1
SPLIT 5
700 g
BATCH 2
SPLITS
9 & 10
75 g EACH
7 - 100 g
FISCHER
ASSAY
SAMPLES
BATCH 1
SPLIT 12
700 g
BATCH 2
SPLITS
23 & 24
75 g EACH
7 - 100 g
FISCHER
ASSAY
SAMPLES

Figure 7. Splitting and blending scheme for OS-1.

ground shale was sized by passing through a 70 mesh stainless steel mechanical sieve. The full 60 lb. of shale feed stock was processed in this fashion. The crushing and grinding operations also blended the bulk sample to some extent. All the crushers and griners were cleaned and portions of shale were processed and discarded before processing the sample.

For each of the three samples, blending and splitting were performed simultaneously by taking each split and recombining and mixing and then splitting again. This was done 5 times on the first two splits and 4 times on the subsequent two splits. The 16 fractions resulting from the splitting were then blended by hand on a polyethylene sheet and two 75 gm samples were taken from each fraction. In the case of the raw shale, 7-100 gm Fischer assay charges were also taken from each 1/16 fraction. What remained of each sixteenth fraction was placed in a polyethylene bottle and labeled Batch 1, split 1-16. The 75g samples were packaged in glass bottles and labeled Batch 2, split 1-32. All bottles were rinsed with 1-1 $HNO_3$ and deionized water and dried before use. The bottled samples have been stored in a sealed polyethylene container in a vault at a constant temperature of $10^{\circ}C$. Figure 7 is a diagram of the splitting scheme for OS-1.

## Comments Concerning Contamination

The steel crushers, grinders and sieves used to process OS-1 can all be a source of contamination to various degrees. A U.S. Geological Survey group, in a study of contamination by steel crushers and grinders, found that Fe can be increased by as much as 1.5 % Ni - 60 ppm, Mo - 20 ppm, V - 10 ppm, Cu - 30 ppm, and Mn - 1000 ppm (11). The main source of contamination appeared to be disc-type metal grinders. Another study on the grinding and sieving of small samples showed that contamination will most likely be inhomogeneous and cause a widely abherrent result in a trace element analysis (12). Stainless steel sieves can contribute about 3 ppm Ni, 3 ppm Mn, and 20 ppm Fe to a sample. Flannagan, in the preparation of the U.S.G.S. standard rocks (13), could detect no contamination from the use of jaw crushers and rollers in those samples. The following is an assessment of the level of contamination introduced during the preparation of OS-1.

First, all implements used were previously used for crushing and grinding oil-shale and were cleaned with some of the sample which was discarded so there is little possibility of cross contamination from previous samples. Processing by the jaw crusher and roller crusher may have added bits of steel in an inhomogeneous fashion but this could be eliminated by passage of a magnet over the powder. The shatterbox actually grinds the sample against itself and when the steel rings are touching, the sound changed and the grinder was stopped and a new charge added. Thus, contamination will be much less severe than that by using steel plates. Contamination could come from the stainless steel sieve. Comparing the levels of contamination mentioned above with those abundances listed in Table I, it is likely that grinding added up to 10% of Ni and Mn to OS-1, up to 5% of Fe, Cu, and Mo, and up to 1% V to the sample.

## Homogeneity Tests

A simple test of the homogeneity of the standard samples has been made using an x-ray fluorescence analysis method for Rb and Sr devised by Doering (14). This method uses rock powder ground to minus 200 mesh packed in a small nylon planchet. The analysis has been calibrated using standards in which the Rb and Sr contents have been analyzed by isotope dilution and yields the Rb/Sr to ±3% at the 95% confidence level and the abundances of Rb and Sr to ±6% at the 67% confidence level.

Eight samples of about 10 g were randomly chosen from eight different 75 g splits of each standard and were ground in Spex Mixer/Mill using a tungsten carbide chamber to -200 mesh. The 24 samples were all analyzed on the same day to eliminate instrument drift and bias in packing the charges in the planchets. The results are summarized on Table II. The mean, range, standard deviation, and relative standard deviation are used according to the definitions prescribed in Analytical Chemistry, 46, p. 2258, 1974. The mass absorption coefficients were determined by making a count of the compton scattered photons at a $2\theta$ angle of $21^{\circ}$.

The range and trend in the values for the mass absorption coefficient directly correlate with the Rb and Sr abundances. Coarser material won't pack as densely into the planchet thus yielding a lower mass absorption coefficient and also a lower value for the abundance of Rb or Sr. Thus, the deviations in the results appear to be caused by grinding and packing and not by true differences in the abundances of the two trace elements in the different splits. The conclusion is corroborated by the fact that the results for the spent shales, which are much finer in grain size, exhibit better precision. The conclusion is that the different splits of all three standard samples are homogeneous to within ±5%.

## Suggestions for Next Time

Grinding the raw shale using the shatterbox is definitely the best procedure unless a large supply of ceramic ball mills are available. Grinding chambers for the shatterbox are also available in tungsten carbide and alumina ceramic. The tungsten carbide would add appreciable Co and a trace of Ti, but it is quite expensive (12). The alumina adds appreciable Al, Co, Ga, and Li and may take longer for grinding (12). Unless money is no problem, contamination by grinding will have to be tolerated.

The contamination by sieving can be eliminated by testing how long it takes to grind a uniform charge to less than 65 mesh in the shatterbox and then grinding for that period of time.

Pulverizing the samples to a smaller grain size such as -200 mesh may release volatile organic fractions and inorganic species such as Hg, $AsH_3$, and $H_2Se$. This possibility increases because of the dusty character of oil-shale, because of the larger surface area of the smaller grains, and because heating of the sample may occur during the longer grinding periods. In any event, tests should be performed on some scrap oil-shale to determine the amount of dust producing and the amount of heating that occurs upon grinding.

## REFERENCES

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## TABLE I

### Mineral and Chemical Composition of Oil-Shale from Core C-230, Mahogany Zone (6)

| Major Elements in Percent | | Trace Elements in ppm | | | |
|---|---|---|---|---|---|
| $SiO_2$ | 28 | Li | 70 | Zn | 80 |
| $Al_2O_3$ | 6.6 | B | 100 | Ga | 10 |
| $Fe_2O_3$ | 3.2 | F | 1200 | As | 30 |
| $MgO$ | 4.0 | Sc | 5 | Se | 1.5 |
| $CaO$ | 7.2 | Ti | 1200 | Sr | 295 |
| $K_2O$ | 1.1 | V | 200 | Y | 10 |
| $Na_2O$ | 1.8 | Cr | 30 | Zr | 60 |
| $P_2O_5$ | 0.2 | Mn | 224 | Mo | 30 |
| Total Sulfur | 1.65 | Co | 12 | Cd | <.6 |
| Ash | 62.1 | Ni | 30 | Sb | 3 |
| | | Cu | 70 | Ba | 300 |
| | | | | La | 45 |
| | | | | Hg | 2.9 |
| | | | | Pb | 43 |

Oil Yield: 68.8 gal/ton

Minerals:

Raw Shale: Quartz, dolomite>> albite, analcime, calcite >>dawsonite

Shale Ashed: Quartz >>dolomite, albite, (anhydrite)

@ 525°C

Table II. Results of homogeneity tests for Rb and Sr on the standard oil-shale and spent-shales.

| | OS-1 | SS-1 | SS-2 |
|---|---|---|---|
| Number of Samples | 8 | 8 | 8 |
| Range for Sr (ppm) | 553-615 | 966-1051 | 747-793 |
| Average for Sr (ppm) | 584 | 1006 | 771 |
| Standard dev. for Sr (ppm) | 24 | 28 | 17 |
| Relative std. dev. for Sr (%) | 4.1 | 2.8 | 2.2 |
| Range for Rb (ppm) | 55.8-63.9 | 66.6-73.8 | 78.6-82.2 |
| Average for Rb (ppm) | 60.1 | 70.2 | 80.7 |
| Standard dev. for Rb (ppm) | 2.7 | 2.1 | 1.5 |
| Relative std. dev. for Rb (%) | 4.5 | 3.1 | 1.9 |
| Range for Rb/Sr | 0.101-0.105 | 0.068-0.071 | 0.101-0.107 |
| Average for Rb/Sr | 0.103 | 0.070 | 0.105 |
| Standard dev. for Rb/Sr | 0.001 | 0.001 | 0.002 |
| Relative std. dev. for Rb/Sr | 1.1 | 1.5 | 2.1 |
| Range for MA* | 7.71-8.43 | 9.91-11.12 | 9.61-10.45 |
| Average for MA | 8.06 | 10.7 | 10.3 |
| Standard dev. for MA | 0.27 | 0.37 | 0.3 |
| Relative std. dev. for MA | 3.3 | 3.5 | 2.8 |

* MA is mass absorption coefficient in $cm^2/gm$

Discussion following Wildeman Presentation -

Question: What do you know about the composition of the flue gas?

Answer: Water, carbon dioxide, carbon monoxide, the ammonia and $H_2S$ are stripped out. Very small amount of oxides of nitrogen. Very little $SO_2$ due to absorption in the spent shale. Some particulates from the grinding action of the ball mill.

Question: Is there organic nitrogen in the shale oil?

Answer: The shale oil contains 1 to 8% Nitrogen.

Question: What happens to the 1% sulfur in the shale and shale oil?

Answer: The sulfur in the oil comes out as $H_2S$ and would be recovered and sold as sulfur. The inorganic sulfur is found mainly in the spent shale.

# MINOR ELEMENTS IN OIL SHALE AND OIL-SHALE PRODUCTS

by R. E. Poluson, J. W. Smith, N. B. Young, W. A. Robb, and T. J. Spedding

Laramie Energy Research Center, Energy Research and Development
Administration, Laramie, WY 82071

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## ABSTRACT

This paper presents order of magnitude analyses for minor elements in several Green River Formation oil shales, shale oils and retort waters. The oil shale analyses are found to be remarkably uniform throughout a wide region. Crude shale oils and retort waters were found to have some large variations in trace elements. The cause of the variations could not be determined from the available data. The need for standard reference materials and methods, along with cooperative testing for oil shale and its products was discussed.

# MINOR ELEMENTS IN OIL SHALE AND OIL-SHALE PRODUCTS

R. E. Poulson, J. W. Smith, N. B. Young
W. A. Robb, and T. J. Spedding[1]

## INTRODUCTION

Accurate analyses of oil shale and its products are important in perfecting control technology for a developing industry and in anticipation of a need for effluent regulation. Both organic and inorganic compounds are of concern, but this paper is limited to only a part of that concern, ie. elemental analyses without regard to particular chemical compounds.

Methods for accurate analysis are not available for all elements of possible concern in oil shale and oil-shale products. In the case of the total oil-shale resource this does not seem a serious deficiency because an accurate analysis of some particular oil shale would probably represent only that material which was analyzed. It is possible that a few feet up or down in the formation, different results would be obtained. Furthermore, it is the biological availability of the oil shale and the oil-shale product constituents which seems more important environmentally than the exact elemental content.

Although accurate minor element analyses on any given oil shale or product may be of small intrinsic importance, the ability to make accurate analyses has an important role in revealing possible routes of biological availability of oil-shale constituents. In a similar way, useful oil-shale processing information may be obtained when routes for unwelcome intrusion of trace elements into sensitive points in processing schemes (catalytic reactors, eg.) may be recognized. One means toward this end is of course the material balance study which must begin with accurate oil-shale sampling and analysis and be completed with comparably accurate product sampling and analysis.

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[1] All authors are with the Laramie Energy Research Center, ERDA, Laramie, WY.

The objective of this paper is to present a large body of data, primarily for information, with emphasis on minor elemental contents of oil shale and oil-shale products and to point out deficiencies in the data. We believe these deficiences indicate the need for standard reference materials with certified analyses for oil shale and oil-shale products, and the need for a cooperative-laboratory analytical program based on those standard materials. The development of techniques giving accurate results should then lead to means for evaluating transport of these minor elements in a processing plant or into an ecosystem.

The data presented are termed survey analyses. By this is meant total elemental analyses except for C, H, N, O, In, and in some cases Re. The data by and large are of order of magnitude precision only. Somewhat better precision was expected with the techniques used, but the data nevertheless serve to show comprehensively the range of elemental contents of oil shale in the Green River Formation Mahogany zone, in a saline zone far below it, and of shale oils and coproduced retort waters derived from Anvil Points, Colorado mine run shale.

Most previous work with Green River oil shale has been limited to selected elements (1, 2, 3, 4, 5)[2] except for that of Cook (6) who presented a survey analysis on a pyrolyzed oil shale. In the present work, survey analyses were made using spark source mass spectrometry (7) for minor elements complemented by various techniques which are more common for major elements and some minor elements.

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[2] Underlined numbers in parentheses refer to references at the end of this report.

## EXPERIMENTAL

### Oil Shales

Two Green River Formation oil-shale zones were sampled for analysis, the Mahogany zone in Colorado and Utah and a saline zone below the Mahogany zone in Colorado. All shale samples were jaw-crushed to between 6" and 1/4" then reduced by core grinding to minus 8 mesh. Samples were reduced to minus 100 mesh in a hammermill and blended in a plastic V-mixer. The source of the 10 Mahogany zone cores is shown in table 1. A more detailed discussion is presented by Smith (2). The saline zone samples were from an 821 foot section from USBM-AEC* Colorado Corehole No. 3 in the Northern Piceance Creek Basin. Samples were composited 10 foot intervals and were (in increasing order of depth) nos. 2, 16, 25, 32, 53, 63, 73, and 83 of reference (8). Sample no. 2 began at 1909 feet below Kelly bushing (elevation 6,397 feet).

Spark source mass spectrometry, neutron activation and X-ray fluorescence analyses were done directly on raw oil-shale powder. The detectability limit for elements in oil shales was taken as 0.1 ppm in the mass spectrometric measurements. The X-ray fluorescence work used goniometric analysis (9). In addition, silicate concentrates were prepared from the Mahogany zone composites by hydrochloric acid treatment, principally to remove carbonates, followed by 500° C ashing prior to X-ray fluorescence analysis. Elemental detectabilities in X-ray fluorescence as used are shown in table 2.

### Shale Oils

Crude shale oils were obtained from retorts listed in table 3 using the indicated oil shales. Oils with "F" suffix were filtered through Whatman 42 paper before analysis. Oils with "U" suffix were unfiltered crude shale oils were pyrolyzed at 450° C before analysis. Mass spectrometric detectability for elements was 0.1 ppm in some runs and 0.01 ppm in others. Footnotes in the data tables indicate which applies in various samples. For oils and waters auxilliary analytical methods were used for major elements and certain minor elements. These methods are listed in table 4.

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## Retort Waters

Retort water was water formed with the oil and decanted from it. The waters were all from the Laramie 10-ton simulated in situ retort. Shales and particle sizes are listed in table 5. Each water was "deoiled" by filtering through diatomaceous earth at 25° C. Subsequent separation of phases on standing and cooling in storage presented an analytical problem. In such cases the "deoiled" water was homogenized before sampling.

Water samples were evaporated to dryness and for mass spectrometry were ashed at 450° C. The radioactivity measurements were made directly on the residue from drying. A pure uranium standard was used. Uncertainties were ±50 percent because of the occurrence of uranium progeny to an undetermined extent.

## RESULTS AND DISCUSSION

As mentioned earlier, an accuracy of a factor of three was expected for mass spectrometric analyses based on results with other materials. It will be seen that order of magnitude is closer to the case for the work at hand. In the discussion of the results for oil shale and oil-shale products, there are not enough data to pinpoint sources of errors. It cannot be determined whether the principal analytical problems are instrumental, sample handling or sample preparation. The data will be discussed showing inconsistencies, consistencies and such conclusions as seen warranted by order of magnitude analyses.

## Oil Shales

Results for Mahogany zone oil-shale samples are shown in table 6. Samples 4A and 5A were prepared as samples identical to 4 and 5 submitted for analysis. If the results for duplicates 4 and 4A and 5 and 5A are considered, and a factor of ten allowed for analytical precision on such a survey type analysis, many results are still outside that boundary. This illustrates the need to determine whether the problem is in sampling or analysis and to develop appropriate methods and materials for standardization.

Results from neutron activation analysis agree qualitatively with the mass spectrometric data. However, the mercury analyses of oil shale by neutron activation analysis, appear not very precise as seen for duplicate analyses on samples 6 and 10.

Except for lead, x-ray fluorescence analysis for raw shale powder in table 7 and silicate concentrates in table 8 agree qualitatively with the spark source mass spectrometry (table 6). Limits of detection by this technique were in many cases well above those of mass spectrometry. Advances in x-ray fluorescence techniques have resulted in improved sensitivities for most elements but no results are currently available.

Alkali metal analyses by flame photometry for both HCl-soluble and insoluble fractions of the Mahogany-zone samples are shown in table 9. These results agree qualitatively with the survey results of table 6 for the major element sodium and for potassium except for sample 5. Results for the minor element lithium agree qualitatively with those of mass spectrometry and seem to be closer to the values for the 4A and 5A samples than to values for 4 and 5.

These data confirm nevertheless the concept that the Mahogany-zone oil shales of table 6 are remarkably uniform in their minor element content over a wide region of the Green River Formation. Variations are no more between different cores than between duplicate samples.

The oil shales in table 10 represent a vertical array in the saline-zone below the Mahogany-zone, covering an interval of over 800 feet. Here also we see little variation in trace elemental concentrations compared to probable analytical uncertainties. Indeed, within those limits the results agree with those for the Mahogany-zone samples.

The analyses of Desborough, Pitman, and Huffman (5) for 33 elements in Mahogany zone and R-4 zone oil shales agree in order of magnitude with results here from the Mahogany and saline zones. The early work of Stanfield, et al (1) stated little variation was observed in 18 minor elements with oil-shale grade (organic content) for six samples from various ledges near the Mahogany marker in the vicinity of Rifle, Colorado. The results of Smith and Stanfield (4) for 12 minor elements in Uinta Basin Utah oil shales are also consistent with the data on Colorado oil shale. The net observation from all this work is the remarkable uniformity in minor elemental composition in Green River Formation oil shales. This is consistent with the theory of Smith concerning the geochemical genesis of Colorado's Green River Formation (10).

## Crude Shale Oils

Table 11 shows survey analyses for crude shale oils from four different retort systems shown in table 3. These oils were subjected to low temperature pyrolysis before analysis in contrast to the oil shales which were run directly. Ancillary standard methods were used for certain elements as shown in table 4. The three oils reported in six columns to the right of table 11 were analyzed with and without filtration. There appears to be no systematic variation of results with filtrations so that it was assumed the differences observed were a result of the sampling and analysis scheme. Here as with the oil shales a factor of ten is required to reconcile most of the analyses for the low level constituents in the filtered and unfiltered samples.

In contrast to the monotonous similarity of oil shales mentioned by Smith (10), shale oils and retort waters have shown some real differences in trace elemental composition. To the far left of table 11 results for two oils, 10T-29U and 10T-31U, from the same retort are shown. Operating parameters were different, but it has not been possible to correlate elemental analysis with the parameters of various runs (11). There appear to be unequivocal differences in trace element contents of these oils, however. The analysis in table 11 shows a 12:0.01 ratio in uranium contents for 10T-31U oil relative to 10T-29U oil. This difference has been confirmed qualitatively by alpha spectrometry. The corresponding retort waters also show elevated uranium contents as will be discussed in the next section.

Another real difference in the oils is the arsenic content. The analysis of the Rock Springs, Wyoming in situ oil shows 0.5 ppm and is the lowest of the five oils analyzed. If we add to this comparison the results of Burger et al (12) showing 40 ppm for a shale oil produced by a proprietary process we see the possibility of nearly one-hundredfold range of arsenic levels in a variety of oils. We will discuss some of the possible causes for trace elemental differences in oil-shale products after we have discussed the retort water data.

## Retort Waters

Table 12 shows survey analyses for retort waters produced in the Laramie 10-ton retort from retorting of shale particle size ranges shown in table 5. No correlation of water properties with retorting parameters was detected (11). Several standard water quality parameters were run by separate laboratories. Parenthetical results in table 12 illustrate anything from fair agreement to gross disagreement in values reported. Here again it is not known whether the problem is sampling or analysis.

The water 10T-31 shows a 4.6:0.023 ratio of uranium content relative to 10T-29 which tends to confirm the similar results with these two oils. The uranium content of the waters was also confirmed with alpha spectrometry. Other waters (produced from this system) have since been found showing radioactivity up to 200 ppm uranium. A major elevation in tin level appears for the 10T-30 water. Most other differences in trace elements appear reconcilable by the uncertainties of the survey analyses.

In summary for retort waters as with the crude shale oils differences are definitely detectable among products even of nominally very similar sources.

## Source of Variations of Trace Elements in Crude Shale Oils and Retort Waters

The existing data for Green River Formation oil shales indicates a widespread uniformity in minor elemental composition. It is surprising that there would be thousandfold differences in trace elemental compositions of oils and waters produced under apparently similar conditions. There are at least three factors in oil-shale retorting which might lead products to differ. The data to date cannot confirm or deny any of these however. First, the minor element composition of the oil shale used may be different in spite of the evidence at hand. Secondly, the retorting processes involved may be different in ways not yet understood. Finally the products themselves may be subject to special external influences after retorting, as for example the incursion of groundwater into an in situ process after the pressure developed in retorting has subsided. The applicability of these factors to the observed uranium and arsenic variations in the products will be considered now.

The occurrence of enhanced uranium content in the 10T-31 products over the 10T-29 products might have been ascribed to particle size either as an effect on retorting or as a separative effect of crushing with uranium being enhanced in the 0-1" fraction. This does not appear to be so because a subsequent run with 3"-6" shale from the same source also showed enhanced uranium content in the products yielding over 200 ppm uranium in the water as determined by alpha spectrometry. More detailed measurements on a well defined system are required to pin down the causes of the variations.

There is an interesting possibility as to the cause of variations in arsenic levels in the various oils. The oil with the lowest value is the Rock Springs, Wyoming Site 4 in situ produced oil which was liberally washed with alkaline groundwater. The proprietary oil mentioned above had the highest arsenic level and was produced in the driest way of any. Using the average of the "U" and "F" values, the other oils in table 11 were intermediate in arsenic levels and in water contact with the 10-ton and 150-ton simulated in situ processes being much wetter than the gas combustion process. Alkaline washing is the basis for some processes for arsenic removal from shale oil (12) and this may be the explanation for this observation. At present an equally valid explanation would be shale source because the in situ oil was from the Green River Basin (Wyoming) of the Green River Formation. Again a more detailed study is necessary to pinpoint variables.

## Suggestions for Further Work

The variability of the oil-shale product trace elemental composition is intriguing with respect to environmental control technology, and raises significant questions. To answer such questions, retorting experiments with material balance assays of the elements of concern will be needed. To help such studies, the analytical methodology for minor elements in oil shale and oil-shale products needs to be improved based on the results we have presented here.

A program such as the National Bureau of Standards Standard Reference Materials (SRM) work seems well suited in helping to develop methodology for attainment of accurate results for oil shale and oil-shale product minor elements. If one looks to the SRM program, reference materials for trace elements in oils and water do exist. These could be useful, with some alteration, in analyses of shale oil and retort water and spent shale if the certification list were extended to include more elements of environmental concern. None of the existing water standards are alkaline, or have organic contents of up to 2% that are characteristic of oil-shale retort waters, or up to 10% occuring in some oil-shale formation waters (11). There is, however, no standard comparable to raw oil shale with respect to its intimate mix of organic and refractory inorganic material. For these reasons it is suggested that work on an SRM for oil-shale liquid products could be an extension of existing standards but for oil shale a new standard would need to be prepared and certified.

The certification of existing standards for oil, water, and ash along with a new standard for raw oil shale should aim at certification of all elements of potential environmental or product developmental concern. It would be useful, for example, to have an oil certified for antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, fluorine, gallium, iron, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, tin, uranium, (with progeny), vanadium, and zinc. Not all of these elements have been reported in shale oils, but traces may occur in oil shales so methods should be available for screening products until the fate of these elements is well understood.

As an adjunct to the preparation of standard reference materials, a cooperative laboratory test program would probably do much to show up problems in application of methodology. In addition to the analysis itself, guidelines in sampling of oil shale and its products will need to be developed before any analytical technology can be applied to a real process. This will require a determination of the degree of heterogenity which might exist with respect to minor elements in oil shale, spent shale, shale oil and associated aqueous phases.

Work in progress at the Laramie Energy Research Center will soon be published on analyses of leach waters from raw and spent shales from the Laramie 10-ton retort runs reported in this paper along with results from other runs. A program on analysis of selected trace elements in runs from the Laramie Controlled-State Retort (13) is being undertaken. The charge to this retort has been riffled at 1/8 to 1/2 in particle size and might be more homogenous than the 10-ton retorting charges.

## SUMMARY

Order of magnitude minor elemental analyses for several Green River Formation oil shales, shale oils, and retort waters were presented. The oil-shale analyses showed a remarkable uniformity between Colorado Piceance Creek Basin Mahogany zone and saline zone oil shales. Comparison with earlier data of other workers extends this uniformity to rich and lean Mahogany zone oil shales, to the Mahogany and R-4 zones of the Piceance Creek (Colorado) and Uinta (Utah) Basins.

Crude shale oils and retort waters were shown to have variations in trace elements of up to 10  even in products from very similar retorting runs. The cause of such variations could not be determined from the data. Possible important variables, postulated but not yet evaluated, are heterogeneity in the oil shale, subtle differences in retorting processes, or special external influences, on the products after retorting.

Survey type analysis were shown to be larger than expected, but the survey analysis with only order of magnitude precision was shown useful in delineating potential problems. The expected gain from more precise analyses was shown to be with respect to differentiating the causes of product variability in oil-shale retorting.

Suggestions for further work were for the generation of an oil-shale standard reference material through the National Bureau of Standards or other program with certification for a list of many elements of potential environmental and processing concern. It was also recommended that existing SRM's for oil, water and ash should be extended in certification for a larger list of elements. A cooperative interlaboratory analysis program was suggested. The need for development guidelines on sampling of oil shale and products was pointed out.

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TABLE 1. - Description of cores and their selected sections

| Core | | | Location | | | | | Selected section | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Source | Name of well | State | County | Sec. | T. | R. | No. of samples | Length[1] ft. | Reference to marker, ft.[2] |
| 1 | Tell Ertl | Phil | Colo. | Rio Blanco | 25 | 1 S. | 100 W. | 84 | 85.5 | 27.5 to -58 |
| 2 | Weber Oil Co. | Marcedus No.2 | Colo. | Rio Blanco | 30 | 3 S. | 98 W. | 56 | 170 | 85 to -85 |
| 3 | Union Oil Co. | Betty | Colo. | Garfield | 21 | 4 S. | 95 W. | 169 | 201 | 76 to -125 |
| 4 | U.S. Bureau of Mines | Naval Hole E | Colo. | Garfield | 2 | 5 S. | 95 W. | 94 | 155 | 54 to -101 |
| 5 | Pacific Oil Co. | Wheeler No. 1 | Colo. | Garfield | 12 | 5 S. | 98 W. | 105 | 111 | 35.4 to -75.6 |
| 6 | U.S. Bureau of Mines | D-5 | Colo. | Garfield | 12 | 6 S. | 95 W. | 84 | 84 | 22 to -62 |
| 7 | Pacific Oil Co. | Dragert No.1 | Colo. | Garfield | 5 | 6 S. | 96 W. | 136 | 143 | 53 to -90 |
| 8 | Pacific Oil Co. | Hardison No.1 | Colo. | Garfield | 2 | 7 S. | 98 W. | 68 | 68 | 17 to -51 |
| 9 | Continental Oil Co. | Corehole No.2 | Colo. | Garfield | 3&4 | 7 S. | 99 W. | 41 | 71.8 | 35 to -36.8 |
| 10 | Shell Oil Co. | Corehole No.2 | Utah | Uintah | 17 | 11 S. | 24 E. | 56 | 56 | 24 to -32 |

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[1] Maximum continuous length of core averaging 25 gallons of oil per ton.

[2] Positive values indicate top of section above the Mahogany marker, negative values indicate bottom of section below the marker.

TABLE 2. - Limits of detectability for various elements in raw oil-shale powder and in silicate concentrates using x-ray fluorescence

| Element | Method[1] | Detection limit, ppm | Element | Method[1] | Detection limit, ppm |
|---|---|---|---|---|---|
| Uranium | A | 13 | Strontium | A | 4 |
| Lead | A | 21 | Rubidium | A | 4 |
| Thallium | A | 21 | Arsenic | A | 5 |
| Gold | A | 22 | Gallium | A | 6 |
| Lanthanum | B | 31 | Zinc | A | 3 |
| Barium | B | 17 | Nickel | A | 3 |
| Cesium | B | 97 | Cobalt | A | 8 |
| Iodine | B | 165 | Manganese | B | 4 |
| Silver | A | 10 | Chromium | B | 3 |
| Molybdenum | A | 4 | Vanadium | B | 4 |
|  |  | Silicate Concentrate |  |  |  |
| Zirconium | A | 4 |  |  |  |
| Titanium | B | 8 |  |  |  |
| Calcium | B | 23 |  |  |  |

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[1] A - LiF crystal analyzer, air path, scintillation counter with pulse height analyzer.
B - LiF crystal analyzer, helium path, gas-flow proportional counter with pulse height analyzer. All elements determined with $K\alpha$ line except I, Cs, Ba, La, Tl, Pb, U with $L\alpha$ line and Au with $L\beta$ line.

TABLE 3. - Sources of crude shale oils

| Symbol | Oil shale retort | Oil shale |
|---|---|---|
| 10T-29 | LERC simulated in situ 10-ton | Colo. 0-1" |
| 10T-31 | LERC simulated in situ 10-ton | Colo. 1-3" |
| 150T-U[1] | LERC simulated in situ 150-ton | Colo. mine run |
| 150T-F[2] | LERC simulated in situ 150-ton | Colo. mine run |
| IS-U[1,3] | Rock Springs Site 4 in situ | Wyo., fractured |
| IS-F[2,3] | Rock Springs Site 4 in situ | Wyo., fractured |
| GC-U[1] | Gas combustion[4] | Colo. 0.25"-3" |
| GC-F[2] | Gas combustion[4] | Colo. 0.25"-3" |

[1] Unfiltered oil.
[2] Oil filtered through Whatman 42 paper.
[3] Oil contained 28% bound water not removable by decantation.
[4] USBM gas combustion retort operated by Colorado School of Mines Research Foundation.

TABLE 4. - Analytical methods used in conjunction with spark source mass spectrometry for oils and water

| Element | Method |
|---|---|
| Calcium, Magnesium | Atomic absorption (AA) |
| Sodium, Potassium | Flame photometry |
| Boron | Colorimetric (Curcumin or Carmine) |
| Chloride | Titration (Silver or Mercury) |
| Fluoride | Specific ion electrode or SPADNS reagent |
| Sulfur | Gravimetric |
| Mercury | Flameless AA (Hatch-Ott) for waters, Flameless atomic fluorescence from gold amalgam for oils |
| Uranium | Alpha spectrometry of natural activity, using a silicon surface barrier detector and 1024 channel pulse height analyzer. Results were ±50% with a detectability of 1 ppm. |

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[1] Distillation to remove organics before this test.

TABLE 5. - Sources of oil-shale retort waters[1]

| Symbol | Oil-shale retort | Oil shale |
|---|---|---|
| 10T-28 | LERC simulated in situ 10-ton | Colo. 0-20" |
| 10T-29 | LERC simulated in situ 10-ton | Colo. 0-1" |
| 10T-30 | LERC simulated in situ 10-ton | Colo. 0-20" |
| 10T-31 | LERC simulated in situ 10-ton | Colo. 1-3" |

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[1] Each water was "deoiled" by filtering through diatomaceous earth.

TABLE 6. - ELEMENTAL ANALYSES OF MAHOGANY-ZONE OIL-SHALE COMPOSITE SAMPLES[1] USING SPARK SOURCE MASS SPECTROMETRY OF RAW SHALE POWDER

| | PPM IN COMPOSITE[2] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAMPLE | 1 | 2 | 3 | 4 | 4A | 5 | 5A | 6 | 7 | 8 | 9 | 10 |
| ELEMENT | | | | | | | | | | | | |
| Uranium | 3.7 | 2.4 | 1.6 | 3.3 | 5.2 | 5.9 | 7.0 | 5.9 | 5.1 | 3.7 | 3.7 | 3.7 |
| Thorium | 1.2 | 1.3 | 1.2 | 1.9 | 12 | 2.0 | 12 | 3.4 | 3.4 | 1.2 | 1.2 | 2.9 |
| Bismuth | <0.10 | <0.10 | <0.10 | <0.10 | 3.5 | <0.10 | 1.7 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| Lead[3] | 1.2 | 1.0 | 1.6 | 2.3 | 14 | 4.4 | 70 | 2.0 | 1.5 | 1.2/ | 6.2 | 2.7 |
| Thallium | <0.67 | 0.72 | <0.67 | <0.59 | 0.80 | <1.1 | 0.40 | <1.1 | <1.1 | <0.67 | <0.67 | <0.67 |
| Mercury[4] | 0.63 | 1.4 | 0.63 | 0.41 | --[6] | 1.4 | --[6] | 0.38, 0.52 | 2.1 | --[6] | 0.93 | 0.31, 0.70 |
| Gold | | | | | | | | | | | | |
| Platinum | | | | | | | | | | | | |
| Iridium | | | | | | | | | | | | |
| Osmium | | | | | | | | | | | | |
| Rhenium[5] | | | | | | | | | | | | |
| Tungsten | <0.03 | 0.03 | 0.09 | 0.03 | 2.1 | <0.04 | 1.1 | 0.06 | 0.14 | <0.03 | <0.03 | 0.09 |
| Tantalum | 0.63 | 0.38 | 0.84 | 1.5 | 0.87 | 1.3 | 1.9 | 1.3 | 1.3 | 1.4 | 0.84 | 3.4 |
| Hafnium | <1.0 | 1.4 | 1.3 | 1.3 | 1.8 | <1.6 | 1.8 | 4.0 | <1.6 | 1.4 | 1.4 | 1.1 |
| Lutecium | <0.07 | <0.08 | <0.07 | <0.06 | 0.38 | <0.11 | 0.21 | <0.11 | <0.11 | 0.07 | 0.10 | <0.07 |
| Ytterbium | <0.24 | 0.32 | 0.80 | 0.30 | 1.6 | 1.3 | 1.6 | 1.3 | 2.5 | 0.80 | 0.80 | 0.80 |
| Thulium | <0.08 | 0.11 | <0.08 | <0.07 | 0.10 | 0.13 | 0.10 | 0.16 | 0.19 | 0.10 | 0.12 | 0.12 |
| Erbium | 0.37 | 0.54 | 0.44 | 1.0 | 0.28 | 1.4 | 0.28 | 0.80 | 0.80 | 0.51 | 0.89 | 0.51 |
| Holmium | 0.18 | 0.20 | 0.37 | 0.16 | 0.33 | 0.29 | 0.33 | 0.29 | 0.29 | 0.27 | 0.18 | 0.37 |
| Dysprosium | 2.4 | 2.6 | 1.7 | 2.1 | 3.9 | 2.7 | 3.4 | 3.7 | 1.8 | 1.9 | 2.4 | 2.4 |
| Terbium | 0.23 | 0.24 | 0.23 | 0.2 | 0.87 | 0.36 | 0.87 | 0.36 | 0.36 | 0.23 | 0.23 | 0.49 |
| Gadolinium | 2.1 | 18 | 2.1 | 1.9 | 0.43 | 3.8 | 0.43 | 3.4 | 3.4 | 2.1 | 2.1 | 4.6 |
| Europium | 0.64 | 0.69 | 0.64 | 0.56 | 2.0 | 1.0 | 1.2 | 1.0 | 1.0 | 0.64 | 0.64 | 0.96 |
| Samarium | 6.5 | 3.3 | 4.6 | 0.93 | 5.6 | 9.0 | 3.3 | 4.8 | 7.2 | 5.1 | 3.0 | 4.6 |
| Neodymium | 25 | 42 | 19 | 23 | 24 | 77 | 24 | 31 | 21 | 26 | 26 | 56 |
| Praseodymium | 18 | 19 | 16 | 16 | 20 | 13 | 9.3 | 13 | 6.6 | 8.3 | 8.4 | 18 |
| Cerium | 110 | 81 | 75 | 66 | 80 | 210 | 80 | 60 | 60 | 75 | 75 | 75 |
| Lanthanum | 50 | 40 | 25 | 22 | 25 | 17 | 25 | 40 | 40 | 25 | 25 | 42 |
| Barium | 680 | 730 | 650 | 700 | 720 | 610 | 750 | 610 | 610 | 680 | 680 | 680 |
| Cesium | 0.07 | 0.07 | 0.07 | 0.06 | 5.7 | 0.10 | 8.5 | 0.24 | 0.10 | 0.15 | 0.15 | 0.15 |
| Iodine | 0.22 | 1.0 | 4.5 | 2.0 | 29 | 0.13 | 1.3 | 0.36 | 0.36 | 0.22 | 0.22 | 450 |
| Tellurium | 0.35 | <0.38 | <0.35 | <0.31 | | <0.56 | | <0.56 | <0.56 | <0.35 | <0.35 | <0.35 |
| Antimony | 0.39 | 0.20 | 0.39 | 0.34 | 3.0 | 0.54 | 5.2 | 0.29 | 0.29 | 0.39 | 0.27 | 0.18 |
| Tin | 2.9 | 1.5 | 2.9 | 1.2 | 3.5 | 4.6 | 2.0 | 11 | 2.2 | 2.9 | 1.4 | 2.9 |
| Indium[5] | | | | | | | | | | | | |
| Cadmium | 0.05 | 0.05 | 0.05 | 0.02 | 1.4 | 0.16 | 1.4 | 0.08 | 0.08 | 0.10 | 0.10 | 0.10 |
| Silver | <0.03 | 0.04 | 0.08 | <0.02 | 1.7 | <0.04 | 0.80 | <0.04 | 0.06 | 0.04 | 0.04 | 0.18 |
| Palladium | | | | | | | | | | | | |
| Rhodium | | | | | | | | | | | | |
| Ruthenium | | | | | | | | | | | | |
| Molybdenum | 14 | 15 | 14 | 12 | 37 | 10 | 37 | 22 | 22 | 14 | 14 | 14 |
| Niobium | 5.2 | 5.6 | 5.2 | 4.6 | 14 | 3.9 | 14 | 8.3 | 3.9 | 5.2 | 5.2 | 5.2 |
| Zirconium | 27 | 29 | 27 | 12 | 60 | 22 | 60 | 22 | 22 | 27 | 14 | 27 |
| Yttrium | 50 | 27 | 50 | 22 | 18 | 40 | 18 | 40 | 17 | 25 | 11 | 38 |
| Strontium | 900 | 730 | 910 | 400 | =2700 | 720 | =2700 | =1400 | 720 | 910 | 460 | 910 |
| Rubidium | 76 | 82 | 110 | 67 | 110 | 120 | 110 | 120 | 120 | 150 | 150 | 450 |
| Bromine | 0.33 | 0.35 | 0.33 | 0.29 | 14 | 1.2 | 28 | 0.52 | 1.2 | 0.76 | 0.57 | 3.3 |
| Selenium ( )[4] | 3.3 (2.2) | 3.5 | 3.3 | 1.3 (2.5) | 2.0 | 5.2 | 3.5 | 5.2 (1.7) | 2.4 | 3.3 | 3.3 | 2.9 (2.0 |
| Arsenic[3] ( )[4] | 18 (36) | 19 | 33 | 86 (22) | 51 | 28 | 23 | 28 (34) | 28 | 18 | 52 | 18 (24) |
| Germanium | 1.0 | 2.6 | 2.1 | 0.91 | 1.9 | 2.9 | 1.4 | 1.7 | 1.6 | 1.0 | 1.1 | 2.1 |
| Gallium | 4.4 | 11 | 10 | 9.0 | 11 | 16 | 11 | 16 | 16 | 10 | 10 | 4.4 |
| Zinc | 4.3 | 9.8 | 9.1 | 8.0 | 60 | 14 | 120 | 14 | 14 | 21 | 21 | 32 |
| Copper | 48 | 29 | 48 | 42 | 120 | 77 | 44 | 77 | 43 | 27 | 48 | 41 |
| Nickel | 380 | 220 | 290 | 330 | 280 | 600 | 150 | 600 | 600 | 760 | 130 | 210 |
| Cobalt | | 8.0 | 7.0 | 8.6 | 11 | | 11 | 12 | 12 | 9.9 | 7.4 | |
| Iron | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Manganese | 190 | 160 | 340 | 190 | 320 | 390 | 180 | 300 | 380 | 220 | 200 | 240 |
| Chromium | 780 | 350 | 970 | 680 | 370 | 770 | 190 | =1000 | 770 | 280 | 280 | 280 |
| Vanadium | 84 | 90 | 180 | 73 | 100 | 130 | 100 | 130 | 280 | 84 | 84 | 84 |
| Titanium | =2600 | =1300 | =2600 | =2000 | =1500 | =4100 | =3100 | =1900 | =4100 | =1200 | =2600 | =1200 |
| Scandium | 3.4 | 16 | 6.9 | 6.0 | 2.7 | 16 | 2.7 | 11 | 5.4 | 69 | 3.4 | 6.9 |
| Calcium | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Potassium | >1% | >0.5% | >0.5% | >1% | >1% | 2.7 | >1% | >1% | >1% | >1% | >1% | >1% |
| Chlorine | 91 | 98 | 250 | 140 | 76 | 220 | 60 | 260 | 260 | 160 | 250 | 340 |
| Sulphur | =2600 | =4900 | =2600 | =1800 | >1% | =1900 | >1% | =4100 | =4100 | =1200 | =2300 | =1800 |
| Phosphorus ( )[4] | 1300 (800) | 650 | 610 | 530 (800) | 4200 | 960 | 2400 | 540 | 960 (530) | 170 | 170 | 340 (460) |
| Silicon | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Aluminum | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Magnesium | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Sodium | >0.5% | =4300 | =4000 | =3500 | >1% | =4400 | >0.5% | >0.5% | =6400 | >0.5% | >0.5% | >0.5% |
| Fluorine | =1200 | =1300 | =1200 | =1000 | =4400 | =3700 | =2100 | =3100 | =1900 | 120 | =2400 | =1200 |
| Oxygen[6] | | | | | | | | | | | | |
| Nitrogen[6] | | | | | | | | | | | | |
| Carbon[6] | | | | | | | | | | | | |
| Boron | 42 | 45 | 42 | 73 | 230 | 110 | 120 | 66 | 66 | 42 | 84 | 84 |
| Beryllium | 2.4 | 0.90 | 2.4 | 2.1 | 0.60 | 3.8 | 0.26 | 1.8 | 5.3 | 2.4 | 1.1 | 5.6 |
| Lithium | 9.2 | 13 | 10 | 3.8 | 160 | 1.9 | 160 | 11 | 6.8 | 6.6 | 18 | 24 |

[1] Samples of about 25 gallon per ton oil shale were composited at -8 mesh, ground to -100 mesh and thoroughly blended. 4A and 5A duplicate 4 and 5.

[2] Elements not reported were below detectability of 0.1 ppm. All elements standardized using National Bureau of Standards, Standard Reference Material (SRM) 1632, a coal, where applicable.

[3] Standarized using NBS-SRM 1633, a coal fly ash.

[4] Neutron activation analysis.

[5] Internal standard.

[6] Not determined.

Reproduced from best available copy.

TABLE 7. - Elemental analysis of Mahogany-zone oil-shale composite samples using x-ray fluorescence of raw shale powder

| | ppm of composite | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Average |
| Element | | | | | | | | | | | |
| Lead | 120 | 130 | 130 | 130 | 120 | 110 | 110 | 97 | 130 | 100 | 118 |
| Barium | 320 | 300 | 300 | 310 | 330 | 300 | 300 | 310 | 300 | 300 | 307 |
| Zirconium[1] | | | | | | | | | | | |
| Strontium | 780 | 850 | 740 | 740 | 790 | 730 | 790 | 790 | 790 | 760 | 776 |
| Rubidium | 63 | 59 | 65 | 67 | 64 | 66 | 65 | 62 | 64 | 60 | 64 |
| Zinc | 39 | 38 | 40 | 41 | 39 | 38 | 38 | 35 | 34 | 35 | 38 |
| Nickel | 130 | 86 | 90 | 120 | 98 | 130 | 97 | 93 | 68 | 70 | 98 |
| Manganese | 420 | 430 | 430 | 440 | 420 | 420 | 410 | 400 | 390 | 420 | 418 |
| Chromium | 300 | 200 | 200 | 310 | 230 | 330 | 230 | 230 | 140 | 170 | 234 |
| Vanadium | 78 | 73 | 78 | 84 | 84 | 78 | 78 | 78 | 78 | 78 | 79 |
| Titanium[1] | | | | | | | | | | | |
| Calcium[2] | | | | | | | | | | | |
| Boron | 53 | 58 | 66 | 76 | 68 | 67 | 66 | 66 | 110 | 136 | 77 |

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[1] Not detectable in raw oil shale under conditions used.

[2] Major element, not determined.

TABLE 8. - Elemental analysis of Mahogany-zone oil-shale composite samples using x-ray fluorescence of oil-shale silicate concentrates

| | ppm of composite | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Average |
| Element | | | | | | | | | | | |
| Lead | 68 | 83 | 88 | 91 | 83 | 82 | 87 | 72 | 81 | 86 | 82 |
| Barium | 140 | 120 | 120 | 130 | 120 | 90 | 100 | 110 | 110 | 100 | 114 |
| Zirconium | 39 | 37 | 41 | 37 | 38 | 41 | 37 | 39 | 33 | 33 | 38 |
| Strontium | 32 | 30 | 33 | 30 | 27 | 20 | 30 | 19 | 22 | 18 | 26 |
| Rubidium | 55 | 59 | 64 | 64 | 62 | 58 | 64 | 48 | 41 | 41 | 56 |
| Zinc | 6 | 6 | 6 | 6 | 7 | 6 | 6 | 6 | 5 | 5 | 6 |
| Nickel | 11 | 10 | 10 | 11 | 11 | 10 | 11 | 10 | 9 | 9 | 10 |
| Manganese | 9 | 7 | 6 | 6 | 8 | 8 | 6 | 8 | 12 | 14 | 8 |
| Chromium | 20 | 15 | 13 | 14 | 12 | 16 | 13 | 17 | 18 | 18 | 15 |
| Vanadium | 66 | 62 | 59 | 59 | 58 | 60 | 54 | 68 | 69 | 76 | 63 |
| Titanium | 1300 | 1300 | 1400 | 1400 | 1400 | 1300 | 1300 | 1300 | 1200 | 1200 | 1300 |
| Calcium | 480 | 420 | 440 | 380 | 410 | 280 | 380 | 290 | 340 | 380 | 380 |
| Boron | 38 | 30 | 37 | 52 | 54 | 52 | 47 | 49 | 77 | 97 | 53 |

TABLE 9. - HCl soluble and insoluble sodium, potassium, and lithium by flame photometry in Mahogany-zone composite cores of Green River oil shale

| Composite | Sodium, ppm |  |  | Potassium, ppm |  |  | Lithium, ppm |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Soluble | Insoluble | Total | Soluble | Insoluble | Total | Soluble | Insoluble | Total |
| 1 | 8270 | 3640 | 11910 | 826 | 11960 | 12786 | 18 | 21 | 39 |
| 2 | 7070 | 4320 | 11390 | 688 | 11510 | 12198 | 17 | 23 | 40 |
| 3 | 4800 | 7650 | 12450 | 664 | 12230 | 12894 | 25 | 18 | 43 |
| 4 | 5180 | 4630 | 9810 | 731 | 12320 | 13051 | 20 | 20 | 40 |
| 5 | 4800 | 3700 | 8500 | 574 | 13810 | 14384 | 16 | 20 | 36 |
| 6 | 5150 | 3480 | 8630 | 1060 | 10980 | 12040 | 59 | 21 | 80 |
| 7 | 4510 | 3030 | 7540 | 635 | 12030 | 12665 | 25 | 18 | 43 |
| 8 | 5640 | 2020 | 7660 | 1080 | 9820 | 10900 | 58 | 21 | 79 |
| 9 | 6140 | 2430 | 8570 | 1770 | 13730 | 15500 | 78 | 10 | 88 |
| 10 | 2530 | 4930 | 7460 | 2120 | 13680 | 15800 | 69 | 11 | 80 |

TABLE 10. - ELEMENTAL ANALYSES OF COLORADO COREHOLE NO. 3 SALINE-ZONE OIL-SHALE COMPOSITE SAMPLES[1] USING SPARK SOURCE MASS SPECTROMETRY OF RAW SHALE POWDER

| | PPM IN COMPOSITE[2] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| SAMPLE | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| ELEMENT | | | | | | | | |
| Uranium | 5.7 | 2.3 | 0.30 | 2.6 | 7.8 | 7.0 | 2.1 | 3.0 |
| Thorium | 13 | 6.9 | 1.6 | 3.2 | 7.6 | 16 | 3.2 | 6.9 |
| Bismuth | 6.1 | 1.7 | <0.52 | 1.5 | 1.4 | 3.5 | 0.65 | 1.7 |
| Lead[3] | 57 | 14 | 1.4 | 7.0 | 16 | 70 | 12 | 14 |
| Thallium | 1.4 | 0.40 | <0.12 | 0.30 | 0.19 | 0.40 | <0.12 | 0.40 |
| Mercury[4] | | | | | | | | |
| Gold | | | | | | | | |
| Platinum | | | | | | | | |
| Iridium | | | | | | | | |
| Osmium | | | | | | | | |
| Rhenium[5] | | | | | | | | |
| Tungsten | 2.9 | 1.1 | <0.32 | 0.46 | 2.4 | 1.1 | 0.46 | 1.1 |
| Tantalum | 1.5 | 0.87 | 0.43 | 0.87 | 4.8 | 0.87 | 0.65 | 0.87 |
| Hafnium | 2.5 | 1.8 | <0.55 | 0.55 | 0.77 | 0.79 | 1.6 | 1.8 |
| Lutetium | 0.41 | 0.21 | <0.15 | <0.15 | 0.17 | 0.19 | 0.17 | 0.50 |
| Ytterbium | 1.3 | 1.2 | <0.49 | <0.49 | 0.68 | 0.70 | 0.61 | 1.6 |
| Thulium | 0.07 | 0.09 | <0.03 | 0.03 | 0.03 | 0.08 | 0.04 | 0.08 |
| Erbium | 0.23 | 0.21 | <0.08 | 0.10 | 0.13 | 0.28 | 0.12 | 0.28 |
| Holmium | 0.44 | 0.16 | <0.05 | 0.07 | 0.36 | 0.33 | 0.16 | 0.16 |
| Dysprosium | 3.1 | 1.8 | <0.27 | 0.90 | 2.0 | 1.8 | 0.90 | 1.8 |
| Terbium | 1.1 | 0.43 | <0.13 | 0.19 | 0.96 | 0.43 | 0.32 | 0.87 |
| Gadolinium | 0.65 | 0.43 | <0.06 | 0.21 | 0.47 | 0.43 | 0.21 | 0.71 |
| Europium | 1.8 | 1.0 | <0.18 | 0.26 | 1.3 | 1.2 | 0.60 | 1.2 |
| Samarium | 5.1 | 3.3 | <0.50 | 1.7 | 3.7 | 3.3 | 1.7 | 3.3 |
| Neodymium | 29 | 18 | 2.4 | 12 | 20 | 20 | 5.1 | 12 |
| Praseodymium | 16 | 4.7 | 0.60 | 4.7 | 10 | 9.3 | 2.0 | 9.3 |
| Cerium | 65 | 40 | 4.0 | 20 | 53 | 80 | 40 | 40 |
| Lanthanum | 20 | 25 | 1.1 | 9.2 | 24 | 37 | 11 | 25 |
| Barium | 680 | 750 | 61 | 130 | 330 | 300 | 300 | 520 |
| Cesium | 9.2 | 5.7 | 0.43 | 1.1 | 2.7 | 5.7 | 5.7 | 11 |
| Iodine | 1.6 | 0.06 | <0.20 | 13 | 2.5 | 0.67 | 0.67 | 2.9 |
| Tellurium | | | | | | 0.11 | | |
| Antimony | 11 | 1.4 | <0.21 | 1.4 | 3.3 | 3.5 | 1.4 | 3.0 |
| Tin | 1.6 | 2.0 | 0.35 | 0.93 | 2.2 | 2.0 | 0.78 | 1.6 |
| Indium[5] | | | | | | | | |
| Cadmium | 0.54 | 0.67 | 0.10 | 0.12 | 0.37 | 0.25 | 0.14 | 0.67 |
| Silver | 0.28 | 0.40 | 0.13 | 0.17 | 0.45 | 0.40 | 0.13 | 0.40 |
| Palladium | | | | | | | | |
| Rhodium | | | | | | | | |
| Ruthenium | | | | | | | | |
| Molybdenum | 30 | 17 | 8.7 | 8.7 | 41 | 87 | 26 | 87 |
| Niobium | 20 | 12 | 1.4 | 3.2 | 7.1 | 14 | 6.4 | 6.4 |
| Zirconium | 49 | 60 | 3.0 | 15 | 56 | 60 | 30 | 30 |
| Yttrium | 14 | 18 | 1.8 | 6.6 | 8.4 | 29 | 7.6 | 18 |
| Strontium | 610 | 750 | 59 | 270 | 830 | 480 | 270 | ≈1400 |
| Rubidium | 92 | 57 | 11 | 31 | 63 | 85 | 57 | 110 |
| Bromine | 23 | 6.0 | 60 | 6.0 | 6.7 | 6.0 | 6.0 | 6.0 |
| Selenium | 1.6 | 0.78 | 0.90 | 1.4 | 2.2 | 2.0 | 1.2 | 4.7 |
| Arsenic[3] | 25 | 13 | 2.6 | 13 | 20 | 23 | 13 | 31 |
| Germanium | 1.5 | 0.80 | 1.9 | 0.37 | 0.89 | 1.1 | 0.56 | 1.9 |
| Gallium | 18 | 11 | 1.1 | 5.0 | 13 | 11 | 4.9 | 11 |
| Zinc | 49 | 60 | 12 | 26 | 20 | 60 | 26 | 26 |
| Copper | 63 | 33 | 22 | 22 | 49 | 78 | 17 | 44 |
| Nickel | 80 | 55 | 83 | 28 | 110 | 98 | 28 | 98 |
| Cobalt | 17 | 4.6 | 1.1 | 4.6 | 0.78 | 21 | 4.6 | 11 |
| Iron | >1% | >1% | 830 | ≈3500 | >1% | >1% | >0.5% | >1% |
| Manganese | 310 | 180 | 9.0 | 34 | 200 | 320 | 90 | 320 |
| Chromium | 130 | 87 | 43 | 65 | 210 | 190 | 43 | 87 |
| Vanadium | 82 | 100 | 10 | 50 | 110 | 100 | 50 | 50 |
| Titanium | ≈1200 | ≈1200 | 150 | 730 | ≈1600 | ≈1500 | 550 | ≈1500 |
| Scandium | 4.4 | 2.7 | | 0.12 | 1.3 | 4.0 | 1.2 | 2.7 |
| Calcium | >1% | >1% | >0.5% | >1% | >1% | >1% | >1% | >1% |
| Potassium | >1% | >0.5% | 800 | ≈1600 | ≈3800 | >0.5% | ≈3400 | >0.5% |
| Chlorine | 230 | 600 | >1% | 280 | 160 | 28 | 35 | 76 |
| Sulphur | >1% | ≈4800 | 480 | ≈4800 | >1% | >1% | ≈4800 | >1% |
| Phosphorus | >0.5% | ≈4200 | 510 | ≈2400 | >0.5% | ≈2400 | ≈1200 | ≈4200 |
| Silicon | >1% | >1% | >1% | >1% | >1% | >1% | >1% | >1% |
| Aluminum | >1% | >1% | >0.5% | >1% | >1% | >1% | >1% | >1% |
| Magnesium | >1% | >1% | >0.5% | >1% | >1% | >1% | >1% | >1% |
| Sodium | >1% | >1% | >1% | >1% | >1% | >0.5% | >1% | >0.5% |
| Fluorine | 840 | ≈1000 | 360 | 360 | ≈1200 | ≈1000 | 560 | ≈1000 |
| Oxygen[4] | | | | | | | | |
| Nitrogen[4] | | | | | | | | |
| Carbon[4] | | | | | | | | |
| Boron | 52 | 58 | 12 | 23 | 65 | 120 | 39 | 64 |
| Beryllium | 0.98 | 1.0 | <0.18 | 0.26 | 0.67 | 1.2 | 0.60 | 2.2 |
| Lithium | 47 | 29 | 5.7 | 29 | 32 | 100 | 29 | 57 |

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[1] Samples were composited from selected 10 foot intervals throughout an 821 foot section from a saline zone below the Mahogany-zone, depth increases 1 through 8.

[2] Elements not reported were below detectability of 0.1 ppm. All elements standardized using National Bureau of Standards, Standard Reference Material (SRM) 1632, a coal, where applicable.

[3] Standardized using NBS-SRM 1633, a coal fly ash.

[4] Not determined.

[5] Internal standard.

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TABLE 11. - ELEMENTAL ANALYSES OF CRUDE SHALE OILS[1] USING SPARK SOURCE MASS SPECTROMETRY

| | PPM IN OIL[2] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ELEMENT / Sample | IOT-29-U | IOT-31-U | ISOY-U | ISOY-F | IS-U | IS-F | CC-U | CC-F |
| Uranium | | 18 | | | | | | |
| Thorium | | | | | | | | |
| Bismuth | 0.046 | 0.026 | 0.30 | | | | 0.32 | |
| Lead | 0.098 | 0.32 | 1.1 | 0.11 | | | 1.8 | 0.13 |
| Thallium | | | | | | | | |
| Mercury[3] | 0.11 | 0.16 | 0.51 | 0.14 | 0.67 | 0.72 | 0.22 | 0.25 |
| Gold | | | | | | | | |
| Platinum | | | | | | | | |
| Iridium | | | | | | | | |
| Osmium | | | | | | | | |
| Rhenium[3] | | | | | | | | |
| Tungsten | 0.021 | 0.24 | | | | <0.12 | 1.3 | <0.14 |
| Tantalum | | | | | | | | |
| Hafnium | | | | | | | | |
| Lutecium | | | | | | | | |
| Ytterbium | | | | | | | | |
| Thullium | | | | | | | | |
| Erbium | | | | | | | | |
| Holmium | | | | | | | | |
| Dysprosium | | | | | | | | |
| Terbium | | | | | | | | |
| Gadolinium | | | | | | | | |
| Europium | | | | | | | | |
| Samarium | | | | | | | | |
| Neodymium | | | | | | | | |
| Praseodynium | | | | | | | | |
| Cerium | | | | | | | | |
| Lanthanum | | | | | | | | |
| Barium | 0.011 | 0.028 | | 0.23 | | | 0.10 | 0.32 |
| Cesium | | | | | | | | |
| Iodine | 0.019 | 0.021 | 0.73 | | | | | |
| Tellurium | | | | | | | | |
| Antimony | 0.018 | 0.016 | | | | | | 0.18 |
| Tin | 0.16 | 0.27 | 1.6 | 0.62 | 3.7 | 0.97 | | |
| Indium[3] | | | | | | | | |
| Cadmium | | | 0.11 | | | | | |
| Silver | | | | | | | | |
| Palladium | | | | | | | | |
| Rhodium | | | | | | | | |
| Ruthenium | | | | | | | | |
| Molybdenum | 0.47 | 0.68 | 14 | 7.2 | 1.8 | 6.3 | 1.4 | 1.0 |
| Niobium | | | | | | | | |
| Zirconium | 0.023 | 0.15 | | | | | | |
| Yttrium | | | | | | | | 0.26 |
| Strontium | | 0.093 | | | | | | 0.20 |
| Rubidium | | 0.013 | | | | | | |
| Bromine | 0.037 | 0.095 | | | | | | |
| Selenium | 0.092 | | 0.35 | 0.17 | 0.10 | 0.20 | 0.32 | 0.54 |
| Arsenic | 4.1 | 6.9 | 3.8 | 2.2 | 0.55 | 0.54 | 8.7 | 53 |
| Germanium | | 0.037 | | | | | | |
| Gallium | | | | | | | | |
| Zinc | 0.56 | 1.2 | 3.5 | 3.8 | 1.7 | 2.2 | 3.6 | 9.4 |
| Copper | 0.087 | 0.15 | 0.42 | 0.11 | 0.55 | 0.54 | 1.5 | 1.5 |
| Nickel | 2.5 | 2.1 | 9.0 | 10 | 55 | 12 | 9.4 | 14 |
| Cobalt | 0.75 | 0.86 | 1.2 | 0.66 | 7.8 | 2.7 | 2.5 | 5.0 |
| Iron | 19 | 33 | 25 | 8.3 | 71 | 64 | 390 | 380 |
| Manganese | 0.013 | 0.044 | 0.11 | | 0.15 | 0.14 | 1.1 | 0.36 |
| Chromium | 0.021 | 0.090 | 0.22 | 0.24 | | 0.28 | 0.23 | 0.33 |
| Vanadium | 1.1 | 9.0 | 0.81 | 0.39 | 0.81 | 0.45 | 0.73 | 2.5 |
| Titanium | 0.052 | 0.89 | 0.33 | 0.36 | 2.1 | 2.0 | 1.6 | 0.50 |
| Scandium | | | | | | | | |
| Calcium[3] | 3.4 | 39 | 2.3 | 0.46 | 5.1 | 2.9 | 17 | 32 |
| Potassium[3] | 0.85 | 5.5 | 3.0 | 3.3 | 2.0 | 1.8 | 4.4 | 2.2 |
| Chlorine[3] | 0.057 | 2.0 | 1.5 | 1.7 | 0.21 | 0.42 | 0.68 | 1.1 |
| Sulphur[3] | 66 | 3.1 | 760 | ≈1700 | ≈2600 | ≈2000 | ≈1600 | ≈2300 |
| Phosphorus | 0.15 | 26 | 1.3 | 0.29 | 0.74 | 0.72 | 1.2 | 4.0 |
| Silicon | 21 | 9.0 | 14 | 5.9 | 4.0 | 14 | 44 | 110 |
| Aluminum | 1.3 | 19 | 0.10 | 0.16 | | 0.43 | 2.1 | 0.52 |
| Magnesium[3] | 0.38 | 2.0 | <1.4 | <1.6 | <0.67 | <1.8 | 99 | <2.2 |
| Sodium[3] | <0.73 | 5.4 | <34 | <37 | <16 | <44 | <71 | <32 |
| Fluorine[3] | 0.071 | 0.10 | 2.7 | 3.0 | | 0.35 | 2.8 | 0.89 |
| Oxygen[4] | | | | | | | | |
| Nitrogen[4] | | | | | | | | |
| Carbon[4] | | | | | | | | |
| Boron[3] | [4] | [4] | 3.8 | 2.1 | 2.9 | 8.6 | 0.79 | 1.3 |
| Beryllium | | | | | | | | |
| Lithium | 0.26 | 0.042 | | | | | 0.15 | 0.11 |

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[1] For description of source see table 3.

[2] Elements not reported were below detectability of 0.01 ppm in IOT-29 and IOT-31 others 0.1 ppm. Oils were ashed at 450° C before M.S.

[3] Determined by alternate methods listed in table 4.

[4] Not determined.

[5] Internal standard.

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TABLE 12. - ELEMENTAL ANALYSES OF OIL-SHALE RETORT WATERS[1] USING SPARK SOURCE MASS SPECTROMETRY

| Sample | PPM IN WATER[2] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 101-28 | | 101-29 | | 101-30 | | 101-31 | |
| ELEMENT | | | | | | | | |
| Uranium | 0.018 (<1)[3] | | 0.023 (<1)[3] | | 0.010 (<1)[3] | | 4.6 (18)[3] | |
| Thorium | | | | | | | 0.013 | |
| Bismuth | | | | | | | 0.001 | |
| Lead | 0.14 | | 0.12 | | 0.062 | | 0.57 | |
| Thallium | | | | | | | | |
| Mercury[3] | <0.1 | | <0.1 | | <0.1 | | 0.10 | |
| Gold | | | | | | | | |
| Platinum | | | | | | | | |
| Iridium | | | | | | | | |
| Osmium | | | | | | | | |
| Rhenium[5] | | | | | | | | |
| Tungsten | 0.003 | | 0.003 | | 0.005 | | 0.024 | |
| Tantalum | | | | | | | | |
| Hafnium | | | | | 0.004 | | 0.002 | |
| Lutecium | | | | | | | | |
| Ytterbium | | | | | | | | |
| Thullium | | | | | | | | |
| Erbium | | | | | | | | |
| Holmium | | | | | | | | |
| Dysprosium | | | | | | | | |
| Terbium | | | | | 0.002 | | | |
| Gadolinium | | | | | | | | |
| Europium | | | | | 0.010 | | | |
| Samarium | | | | | 0.003 | | | |
| Neodymium | 0.005 | | 0.002 | | 0.003 | | 0.001 | |
| Praseodymium | | | 0.003 | | 0.004 | | | |
| Cerium | 0.001 | | | | 0.003 | | 0.004 | |
| Lanthanum | 0.003 | | 0.010 | | 0.005 | | | |
| Barium | 0.002 | | 0.012 | | 0.081 | | 0.077 | |
| Cesium | 0.005 | | 0.002 | | 0.005 | | 0.002 | |
| Iodine | 0.23 | | 0.005 | | 0.33 | | 0.003 | |
| Tellurium | | | | | | | 0.001 | |
| Antimony | 0.005 | | 0.009 | | 0.004 | | 0.036 | |
| Tin | 16 | | 8.9 | | >100 | | 29 | |
| Indium[5] | | | | | | | | |
| Cadmium | | | | | | | | |
| Silver | 0.23 | | | | 0.17 | | 0.002 | |
| Palladium | | | | | | | | |
| Rhodium | | | | | | | | |
| Ruthenium | | | | | | | | |
| Molybdenum | 0.13 | | 0.056 | | 0.057 | | 0.34 | |
| Niobium | | | 0.001 | | | | 0.005 | |
| Zirconium | 0.042 | | 0.079 | | 0.008 | | 0.39 | |
| Yttrium | | | | | 0.050 | | | |
| Strontium | 0.003 | | 0.007 | | 0.025 | | 0.48 | |
| Rubidium | 0.085 | | 0.036 | | 0.062 | | 0.59 | |
| Bromine | 0.18 | | 0.019 | | 0.66 | | 0.13 | |
| Selenium | 0.071 | | 0.010 | | 0.18 | | 0.003 | |
| Arsenic | 4.6 | | 5.9 | | 10 | | 6.4 | |
| Germanium | 0.001 | | 0.001 | | 0.001 | | 0.007 | |
| Gallium | | | | | | | | |
| Zinc | 0.47 | | 0.26 | | 0.43 | | 0.33 | |
| Copper | 0.007 | | 0.008 | | 0.007 | | 0.016 | |
| Nickel | 0.37 | | 1.1 | | 2.6 | | 0.60 | |
| Cobalt | 0.002 | | 0.074 | | 0.32 | | 0.05 | |
| Iron | 9.6 | | 77 | | 26 | | 66 | |
| Manganese | 0.098 | | 0.042 | | 0.14 | | 0.14 | |
| Chromium | 0.013 | | 0.011 | | 0.037 | | 0.017 | |
| Vanadium | 0.004 | | 0.037 | | 0.32 | | 11 | |
| Titanium | 0.75 | | 0.64 | | 2.1 | | 21 | |
| Scandium | | | | | | | | |
| Calcium[3] | 36 | (5.4) | 0.41 | (0.6) | 0.70 | (0.7) | 0.5 | (9.8) |
| Potassium[3] | 16 | (21) | 3.4 | (8) | 12 | (6) | 33 | (70) |
| Chlorine[3] | - | (5500) | - | | - | (6500) | - | |
| Sulphur[3] | 34 | (660) | 14 | (530) | >100 | (430) | >310 | (530) |
| Phosphorus | 1.4 | | 0.58 | | 1.0 | | 9.2 | |
| Silicon | 4.0 | | 1.7 | | 3.5 | | 11 | |
| Aluminum | 0.13 | | 0.11 | | 0.18 | | 0.66 | |
| Magnesium[3] | 47 | (55) | 5.4 | (3.2) | 34 | (5.9) | 87 | (280) |
| Sodium[3] | 64 | (320) | 0.3 | (210) | 14 | (210) | 130 | (1300) |
| Fluorine[3] | 54 | (50) | 34 | (31) | 14 | | 42 | (24) |
| Oxygen[4] | | | | | | | | |
| Nitrogen[4] | | | | | | | | |
| Carbon[4] | | | | | | | | |
| Boron[3] | 4.4 | | 5.2 | | | | 8.8 | |
| Beryllium | | | | | | | | |
| Lithium | 0.004 | | 0.035 | | 0.32 | | 0.75 | |

[1] For description of source see table 5.
[2] Elements not reported were below detectability limit of 0.001 ppm. Waters were evaporated to dryness and run directly.
[3] Determined by alternate methods listed in table 4. Numbers in parentheses from another laboratory.
[4] Not determined.
[5] Internal standard.

Comments following Mr. Poulson's talk.

Comment: The mercury analysis is on raw oil by atomic absorption, most other elements are done on ashed oil.

Comment: For water and oil separation you just decant. Oil in water removed by filtering through wad of cellite to take out the oil globules.

Comment: A standard oil shale would be useful in determining where various materials go in the process. More standardized methods are needed, for example how to define oil and water phases.

# LOW-TEMPERATURE SPECTROSCOPIC ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS

E. L. Wehry, G. Mamantov, R. R. Kemmerer, R. C. Stroupe, H. O. Brotherton,
E. R. Hinton, Jr., P. T. Tokousbalides, and R. B. Dickinson, Jr.

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916

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E. R. Hinton, Jr., P. T. Tokousbalides, and R. B. Dickinson, Jr.

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

## A. INTRODUCTION

The possibility that oil shale processing may cause release of significant quantities of polycyclic organic matter (POM) into the atmospheric and/or aquatic environment has received consideration in the past and will receive greatly increased attention as a shale oil industry begins to develop. In "ex situ" retorting of oil shale, significant amounts of POM are found to be present in both the gaseous and liquid products of the retorting operation.[1] In addition, the spent shale (which, it is envisioned, may be deposited as fill into natural canyons in such areas as the Piceance Creek basin in Colorado) contains significant quantities of POM, which may slowly volatilize into the air or be leached by water.[2] Some POM release may also be anticipated from "in situ" retorting operations.[2] Consequently, assessment of the environmental impact of oil shale refining will require the availability of analytical methodology for identifying, and quantitatively determining, individual polycyclic hydrocarbons.

The analytical chemistry of POM resulting from fossil fuel refining and use is an extraordinarily complex problem, and it seems obvious that no single technique, or group of techniques, will be a panacea. Our efforts have been directed to exploration of the feasibility of using low-temperature Fourier transform infrared spectroscopy, low-temperature steady-state fluorescence spectroscopy, and time-resolved fluorometry in the analysis of POM. In all of this work, we are strongly emphasizing the mode of sample preparation commonly known as matrix isolation.

## B. MATRIX ISOLATION

In matrix isolation (MI) spectroscopy, the sample (in the vapor phase) is mixed with a large excess of an "inert" gaseous diluent, such as $N_2$ or Ar. The gaseous mixture is then deposited upon a cold (*ca*. 20 °K) optical surface; the quasicrystalline deposit is then examined spectroscopically.[3] The objectives of MI include:

(a) To minimize solute-solute interactions, in order that predictable quantitative relationships (*e.g.*, Beer's law in absorption spectrophotometry) be satisfied.

(b) To minimize matrix-solute interactions, in order that the observed spectral band widths be minimized and resolution enhanced - obviously a critical requirement in the analysis of complex mixtures.

(c) To eliminate, whenever possible, contact of samples with liquid solvents, which may introduce contaminants (a problem of particular concern with very sensitive techniques, such as fluorometry).

Inasmuch as most polynuclear aromatic hydrocarbons are rather volatile, converting then to the vapor phase is feasible by vacuum sublimation.[4] A sample cell for vacuum sublimation-Knudsen effusion is shown in Figure 1. The sample is placed in the small glass tube shown at the left of the Figure; this tube, which contains a small (½ mm) orifice at the left-hand end, is heated resistively. This cell is attached to an evacuable cryostat head (*cf*. Figure 2) via the 29/42 male glass joint at the right in Figure 1.

The cryostat head is in turn attached to a commercial closed-cycle helium refrigerator, capable of operation in the 15-20 °K range; the mount for the optical surface upon which the sample is deposited is attached to the body of the refrigerator. The entire assembly (Figure 3) can be inserted into virtually any spectrometer having a cell compartment which opens at the top.

## C. FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy has received virtually no use in POM analysis[5], owing to (*inter alia*) the following difficulties:

(a) Insufficient sensitivity, requiring use of large or concentrated samples (in which case Beer's law is unlikely to obtain) and lengthy spectral scan times;

(b) Optical problems (due to lack of IR transparency of most solvents or solid matrices); and

(c) The complexity of the IR spectra of many polycyclic hydrocarbons, signifying that analyzing the spectrum of a complex mixture may be difficult or impossible.

The first two of the problems cited above can be greatly alleviated by use of the Fourier transform (FT) procedure for obtaining IR spectra, and the third can be at least partially overcome by MI. FT-IR is a "multiplex" spectroscopic technique; *i.e.*, all "resolution elements" of a spectrum are viewed simultaneously by the detector[6-9], in contrast to the conventional sequential scanning technique, wherein the resolution elements are viewed one at a time. In IR spectroscopy, wherein detector dark noise is normally appreciable, multiplexing results in a significant increase in signal-to-noise ratio, which can be utilized either to examine samples too small to study by conventional scanning spectrometry, or to obtain spectra in much shorter times than are conventionally feasible. For example, we have obtained IR spectra of 50 nanomole quantities of polycyclic hydrocarbons with little difficulty by FTS-IR, and a single FTS-IR spectral scan at a resolution of 8 $\text{cm}^{-1}$ requires only 20 sec. Consequently, S/N enhancement by repetitive signal averaging is widely employed in FT-IR measurements.

The process of converting the "raw data" (optical interferograms) of an FT spectrometer to absorption spectra involves a Fourier transformation performed by computer. A digital computer is normally an integral component of a FT spectrometer. This fact signifies that a number of data-handling operations, such as storage of spectra of standard reference materials, background subtraction, and scale expansion are readily executed. In addition, spectra of standards can be compared with those of real sample mixtures; the techniques of pattern recognition[10] can in principle be employed to identify specific sample components. Once individual components have been identified, they may be subtracted ("stripped") from the spectrum of a mixture[11], an operation which, in essence, can be regarded as a form of "chemical separation by computer". All of this assumes, however, that standard reference samples of the various sample constituents exist, a situation which does not obtain at present.

The combination of MI sampling and FT-IR measurement is currently being explored intensively in our laboratory. An example FT-IR spectrum of a three-component mixture is shown in Figure 4. It should be noted that the three constituents (chrysene, benz(a)anthracene, and triphenylene) are isomeric; they are difficult to separate by gas or liquid chromatography and virtually impossible to resolve in a mixture by mass spectrometry.[12] The three individual compounds are readily detectable in the FT-IR spectrum, suggesting that FT-IR will prove to be very useful for examining groups of closely related compounds present in fractions obtained in the liquid chromatography of synthetic fuels.

## D. LOW-TEMPERATURE FLUORESCENCE SPECTROMETRY

Fluorescence spectrometry has been widely employed in the analysis of POM[13], because of its high sensitivity, yet the technique, as conventionally performed, is not well suited for the analysis of complex mixtures, for two principal reasons:

(a) Electronic spectra tend to be relatively broad and featureless, especially in liquid solution, causing severe spectral overlap; and

(b) Energy transfer and quenching phenomena, which can occur over distances which are large by comparison with molecular diameters, can cause the "analytical response factor" for one solute to be dependent upon the identities and concentrations of other solute species present in the sample.

Each of these problems can be reduced in severity by use of low-temperature matrices. Fluorescence spectroscopy in frozen solutions of organic fluorophores has received considerable attention in the past; matrix isolation fluorescence spectroscopy has received much less study. We are currently engaged in a comparative study of frozen-solution and matrix-isolation fluorometry and phosphorometry of POM. Spectral resolution is significantly greater in either frozen solutions or frozen rare-gas matrices than in fluid media; _cf_. Figures 5 and 6 for a comparison of the liquid-solution and MI fluorescence spectra of anthracene.

Though it is premature to state definitive conclusions, it appears that frozen solutions may tend to provide superior spectral resolution to MI, particularly if "Shpol'skii matrices"[14] or "monocrystalline frozen solutions"[15] are employed. However, frozen-solution spectroscopy is very susceptible to quantitative imprecision, owing to microcrystallite formation and aggregation of solute species upon freezing.[16] There is reason to believe that MI, which is not susceptible to such effects, will be the preferred technique for low-temperature quantitative fluorometry.

In order to "isolate" solute molecules from each other for fluorescence spectroscopy in a low-temperature solid matrix, the sample-to-matrix ratio must be very small (perhaps _ca_. 1:5000). It is particularly important to employ very dilute samples in order to minimize the effects of long-range energy transfer, which is often very efficient in mixtures of arenes.[17] Thus, very sensitive detection systems (high-gain photomultipliers; photon counting) may be required, and freedom of the matrix from luminescent impurities is absolutely crucial.

In this respect, MI is clearly superior to frozen-solution spectroscopy; it is much easier to remove fluorescent organic impurities from argon or nitrogen than from n-octane or tetrahydrofuran.

## E. TIME-RESOLVED FLUOROMETRY

It is often asserted (correctly) that emission measurements are inherently more selective than absorptiometry, because there are two wavelength parameters in an emission measurement but only one in absorption. Less widely recognized is an additional parameter - time - which can be employed in emission, but not in absorption, to seek additional resolution of mixtures. The luminescence decay times for organic molecules are finite (*ca*. 10 nsec for fluorescence and *ca*. 1 msec for phosphorescence). Consequently, if the luminescence spectra of two solute species cannot be resolved spectrally, it is conceivable that they can be resolved in the time domain, if their luminescence decay times differ appreciably.

Time-resolved phosphorometry is a well-established procedure[18]; time-resolved fluorescence experiments are more difficult to perform because of the nanosecond decay times. The recent development of laser systems (modelocked cavity-dumped ion lasers[19] and synchronously pumped dye lasers[20]) which can produce subnanosecond pulses at repetition rates variable from 100 MHz to single shot, together with development of detection and transmission-line systems which can operate in the gigahertz frequency region[21], signify that time-resolved fluorescence spectroscopy is now a feasible technique in analytical chemistry.

We are currently engaged in construction and evaluation of a time-resolved fluorometer, shown in block-diagram form in Figure 7. The principal component of the instrument is a modelocked, cavity-dumped argon ion laser, which, when frequency-doubled, will produce 1 nsec pulses at 2573 Å (where virtually all polynuclear hydrocarbons absorb) at repetition rates as great as 100 MHz. The basic electronic readout device is a sampling oscilloscope which, with relatively minor modifications, can be made to function in a manner analogous to a boxcar integrator signal averager.[21] Both fluorescence decay times (intensity vs. time at a fixed wavelength) and time-resolved fluorescence spectra (intensity vs. wavelength at a fixed "time window", 75 ps wide, following firing of the laser) can be acquired with an instrument of this type.

The performance of time-resolved MI or frozen-solution fluorometry should, by concomitant use of spectral and temporal resolution, extend the applicability of fluorescence assay to complex samples of structurally similar molecules.

## F. REQUIRED STANDARD MATERIALS

In recognition of the theme of this Workshop, it is appropriate to conclude this paper with a brief statement of our views pertaining to SRM's. In all of our studies, a "reference library" of spectral data (FT-IR spectra, luminescence spectra, fluorescence decay times) must be acquired before any useful studies of "real samples" can be carried out. At present, in the specific field of POM analysis, many of the most important (carcinogenic) compounds cannot be acquired from commercial sources; in fact, significantly fewer of these materials are commercially available now than in 1970! Those materials which are available are often of questionable purity. There do not appear to exist well-defined channels for obtaining these materials from non-commercial sources.

We would contend that there is a very significant need for SRM samples of the important polycyclic aromatic hydrocarbons, having definite, known purity, available to a wide variety of workers by well-defined, well-publicized channels. Until such a situation is achieved, research in the analytical chemistry of POM will be significantly hindered. Eventually, SRM's of shale oil (and other synthetic fuels) must be made available, but we find it difficult to believe that such SRM's will be of widespread utility until SRM's of the individual components of synthetic fuels exist.

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FIGURE CAPTIONS

Figure 1. Cell for vacuum sublimation-Knudsen effusion of polycyclic hydrocarbons.

Figure 2. Knudsen cell assembly attached to cryostat head.

Figure 3. "Complete" refrigerator assembly, for operation at 15-20 °K, with head and Knudsen cell assembly attached. This is a closed-cycle refrigeration system; no liquid refrigerants are used.

Figure 4. MI FT-IR spectrum of equimolar mixture of three isomeric polycyclic hydrocarbons (chrysene, benz(a)anthracene, triphenylene).

Figure 5. Liquid solution fluorescence spectrum of anthracene.

Figure 6. MI fluorescence spectrum of anthracene.

Figure 7. Block diagram of time-resolved fluorometer. The laser can also be operated in the CW mode. Thus, a high-resolution emission monochromator is employed, so that the same optical arrangement can be employed for both time-resolved and steady-state (conventional) fluorometry.

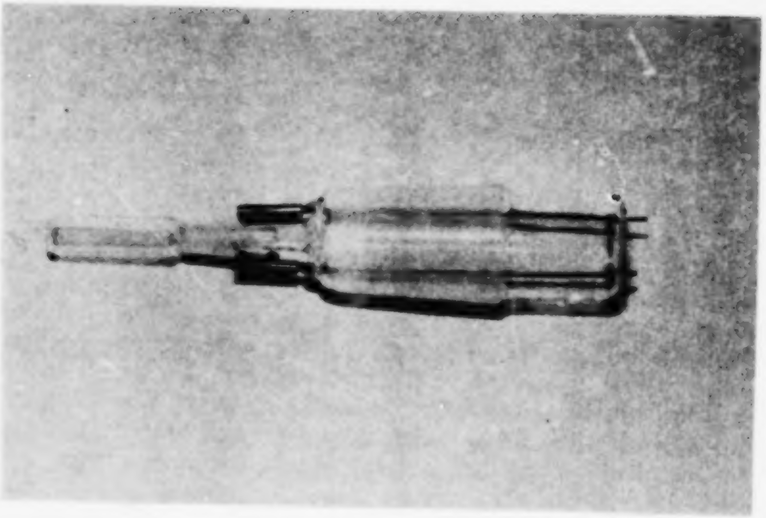


FIGURE 1

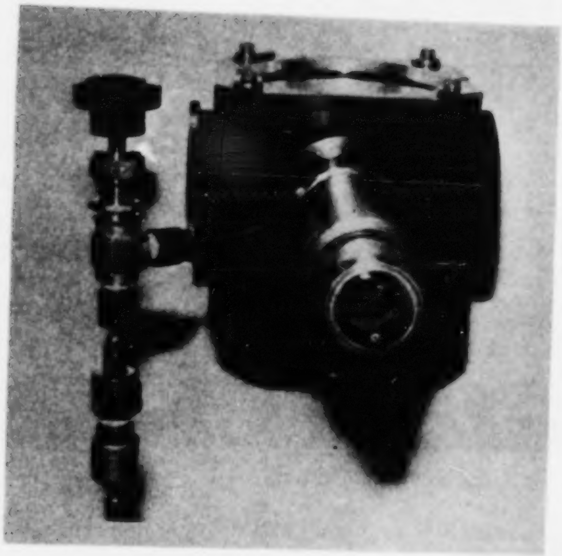


FIGURE 2

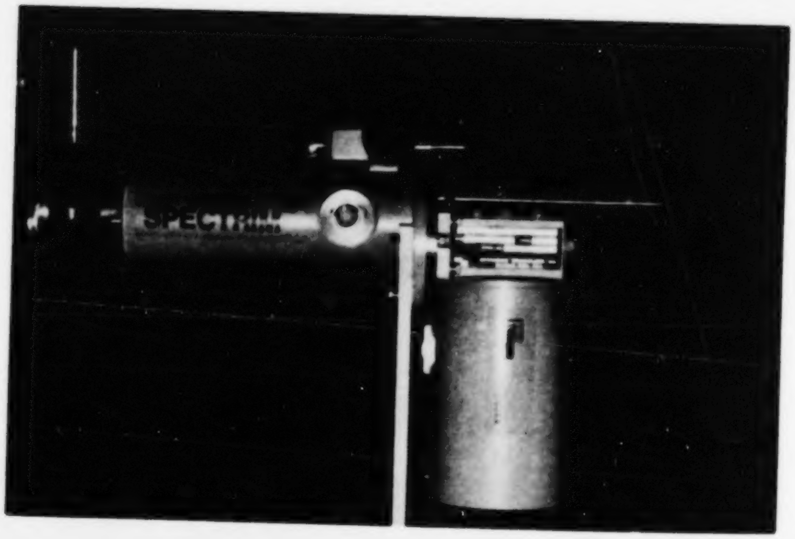
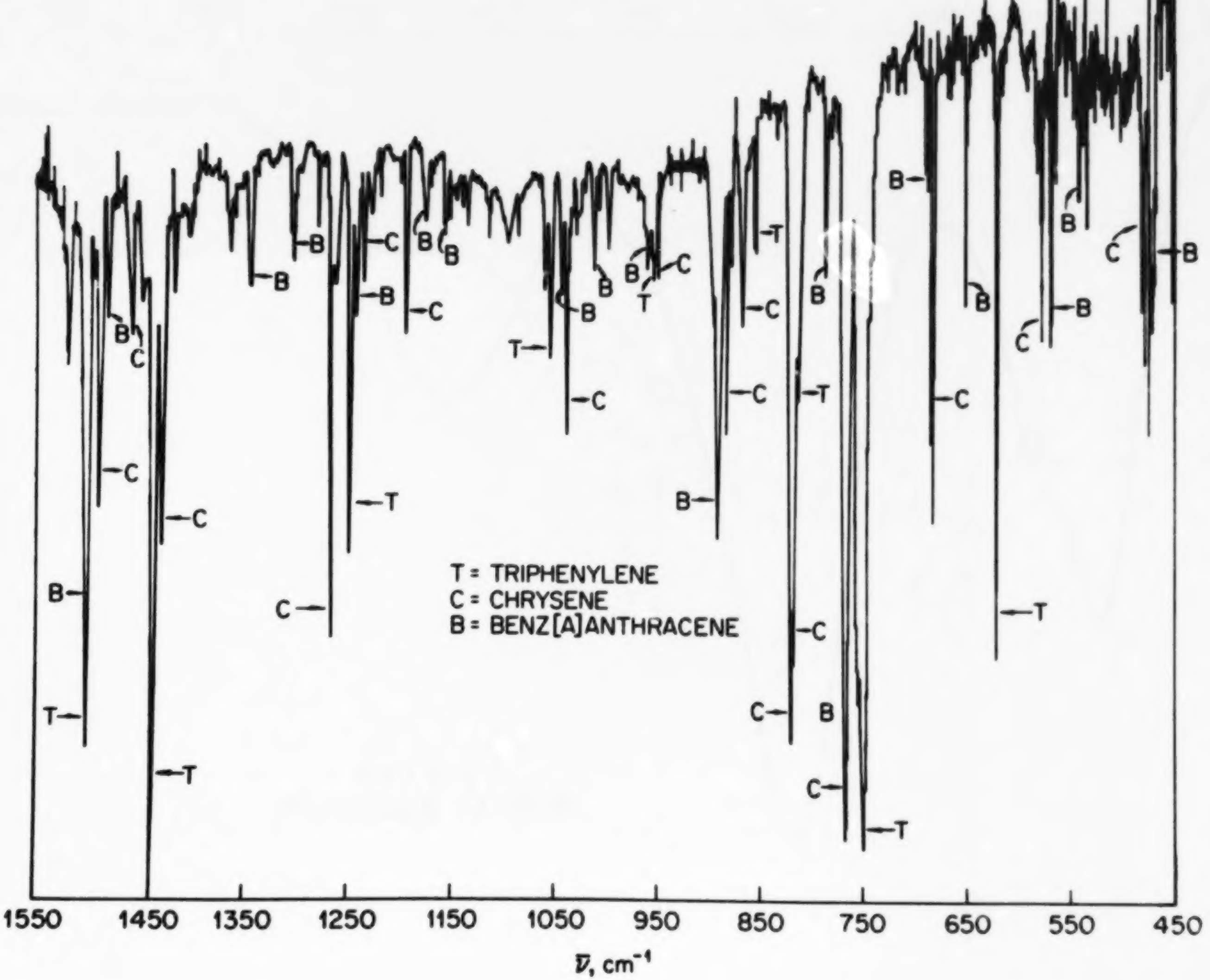
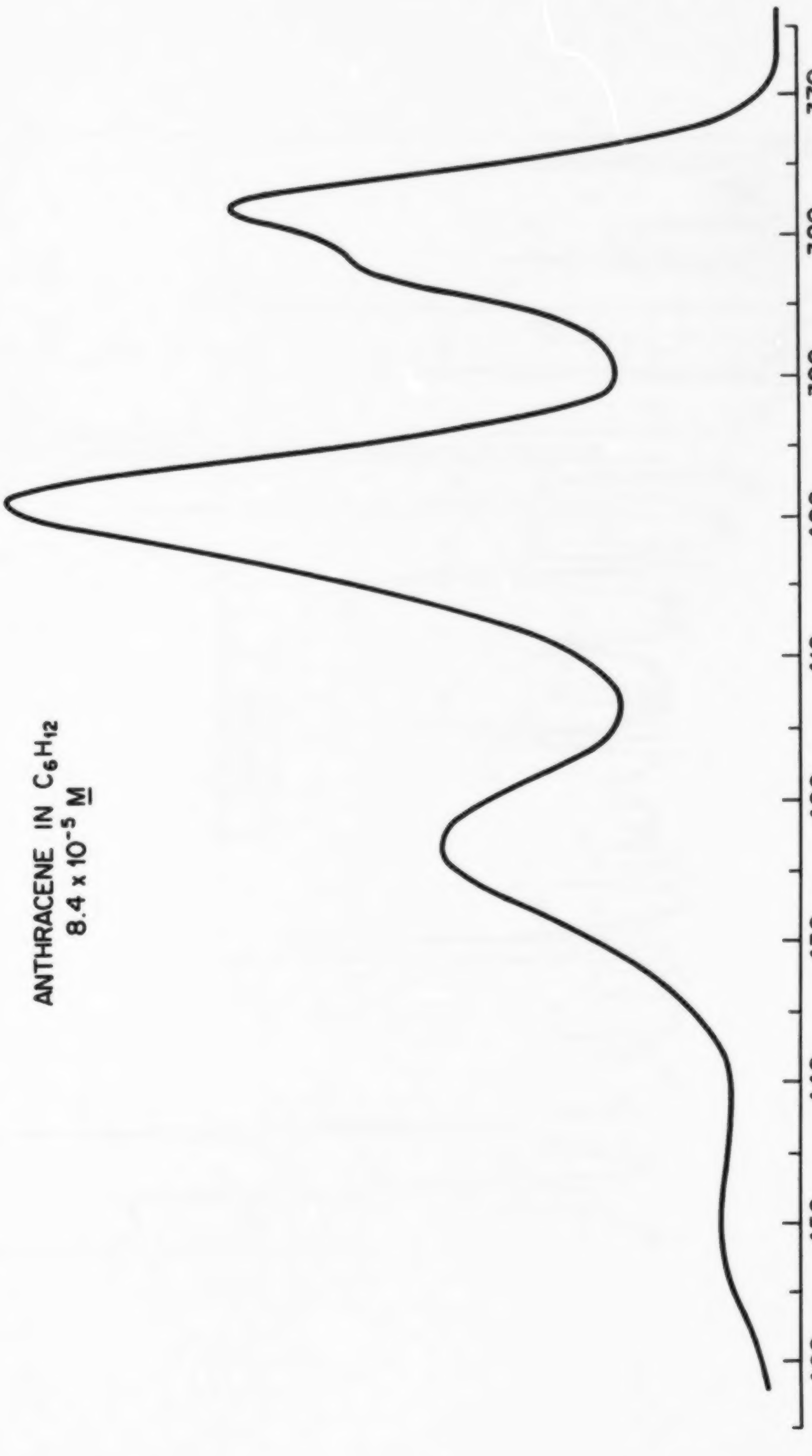
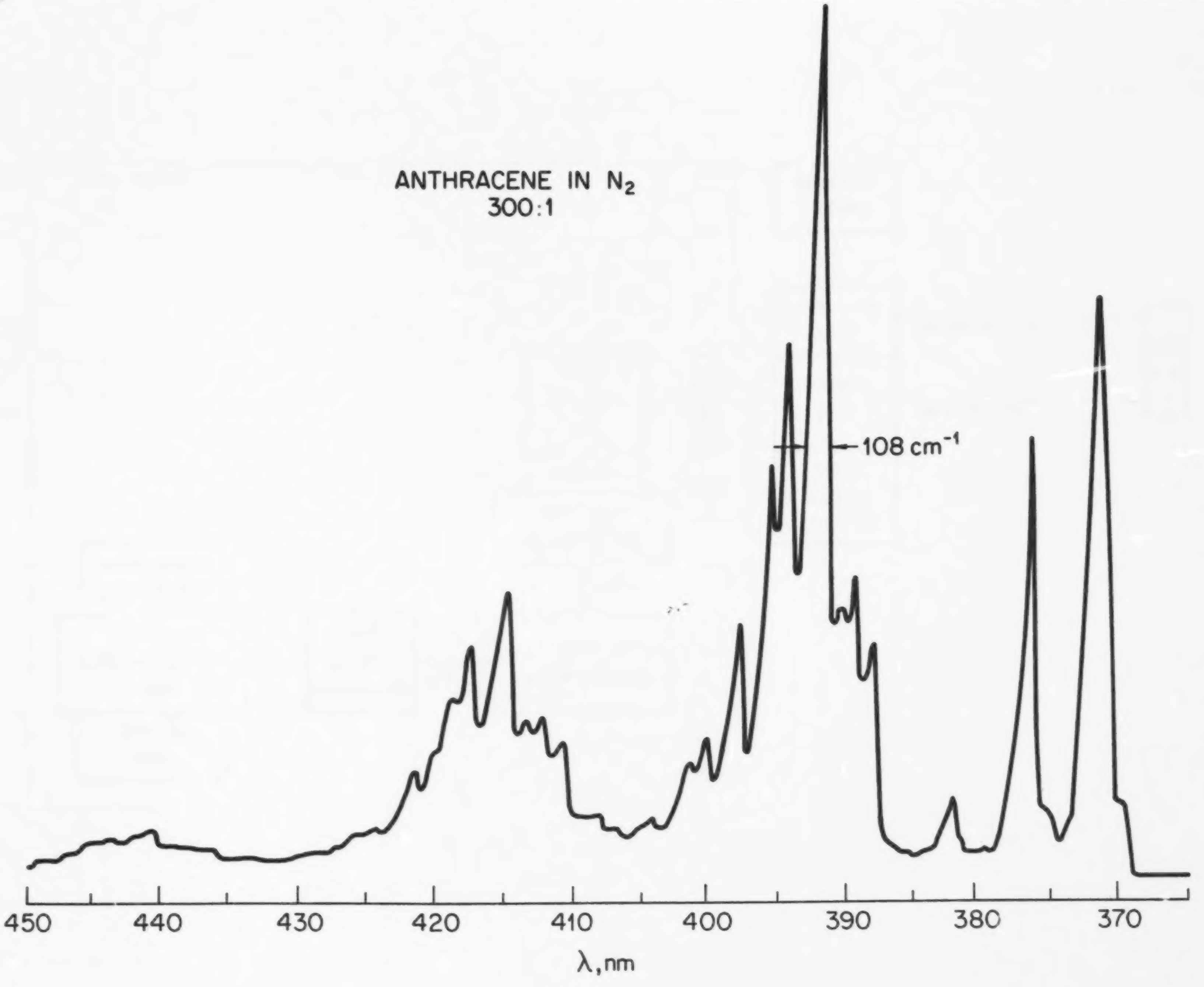


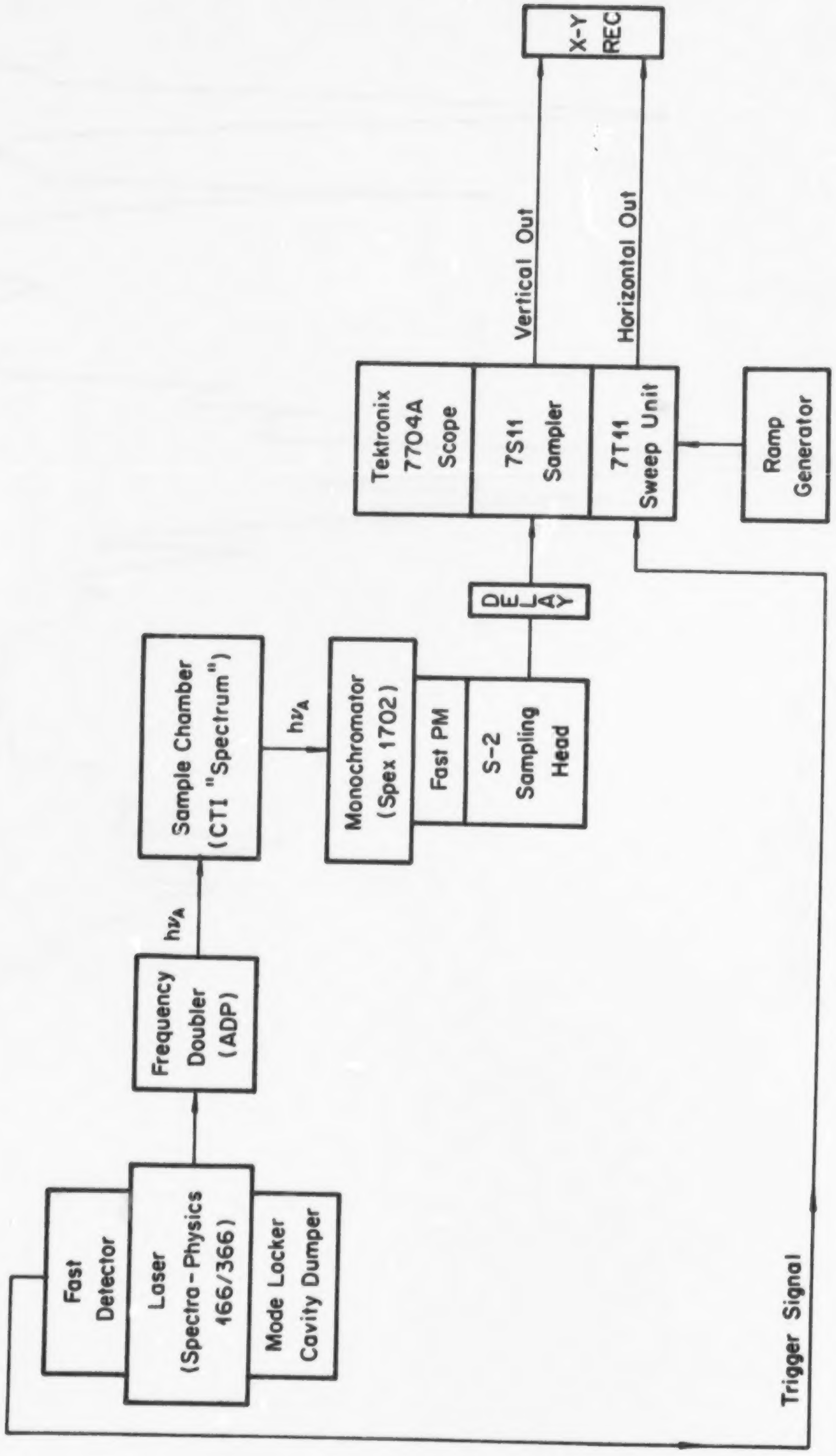
FIGURE 3

$C_{18}H_{12}$ Mixture
TRIPHENYLENE, CHRYSENE, BENZ[A]ANTHRACENE / $N_2$ MATRIX
MATRIX : SAMPLE = 250
EQUIMOLAR MIXTURE - 1 mg of each




ANTHRACENE IN $C_6H_{12}$
$8.4 \times 10^{-5}$ M
370
380
390
400
410
420
430
440
450
460
λ, nm


ANTHRACENE IN $N_2$
300:1
108 cm$^{-1}$
450
440
430
420
410
400
390
380
370
λ, nm


Fast Detector
Laser (Spectra-Physics 166/366)
Mode Locker Cavity Dumper
Frequency Doubler (ADP)
$h\nu_A$
Sample Chamber (CTI "Spectrum")
$h\nu_A$
Monochromator (Spex 1702)
Fast PM
S-2 Sampling Head
DELAY
Tektronix 7704A Scope
7S11 Sampler
7T11 Sweep Unit
Ramp Generator
Vertical Out
Horizontal Out
X-Y REC
Trigger Signal

Comment following Wehry's talk.

Comment: Your technique sounds very informative. The main problem I see is the need for pure compounds to define the individual spectra. For shale oil just determining the compounds present in several hundred peaks, determining each and preparing in a pure form would appear to be a near impossible job.

# APPENDIX B

## Information on Existing NBS-SRM's Useful for Characterizing Oil Shale/Products

U. S. Department of Commerce
Alexander B. Trowbridge,
Secretary

National Bureau of Standards
A. V. Astin, Director

# Certificate of Analysis

## Standard Reference Material 1621

## Sulfur In Residual Fuel Oil

**Sulfur Content..........1.05±0.02 weight percent**

This Standard Reference Material is intended as an analytical standard in the determination of sulfur in residual fuel oil. It is a commercially available oil having the following inspection properties which are supplied for identification only: gravity, 22.6° API; flash point, 136 °F; furol viscosity at 122 °F, 21 seconds; pour point, 40 °F; Ramsbottom carbon residue, 3.3 percent; ash, 0.02 percent; water, not detected; and sediment 0.01 percent.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method used is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 30 determinations and allowances for known sources of possible error.

The oil sample was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Sulfur analyses were performed by B. S. Carpenter, R. A. Paulson, and W. P. Schmidt of the Microanalysis Section.

WASHINGTON, D. C. 20234
December 11, 1967

W. Wayne Meinke, Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Alexander B. Trowbridge,
Secretary

National Bureau of Standards
A. V. Astin, Director

# Certificate of Analysis

## Standard Reference Material 1622

## Sulfur In Residual Fuel Oil

**Sulfur Content..........2.14±0.01 weight percent**

This Standard Reference Material is intended as an analytical standard in the determination of sulfur in residual fuel oil. It is a commercially available fuel oil having the following inspection properties which are supplied for identification only: gravity, 16.9° API; flash point, 152 °F; furol viscosity at 122 °F, 186 seconds; pour point, 30 °F; Ramsbottom carbon residue, 11.9 percent; ash 0.05 percent; water, not detected; and sediment 0.01 percent.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method used is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 17 determinations and allowances for known sources of possible error.

The oil sample was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Sulfur analyses were performed by B. S. Carpenter, R. A. Paulson, and W. P. Schmidt of the Microanalysis Section.

WASHINGTON, D. C. 20234
December 11, 1967

W. Wayne Meinke, Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

# Certificate of Analysis

## Standard Reference Material 1623

### Sulfur in Residual Fuel Oil

**W. P. Schmidt and R. A. Paulson**

Sulfur Content . . . . . . . . 0.268 ± 0.004 weight percent

This Standard Reference Material is an analytical standard for determining sulfur in residual fuel oil. It is a commercially available fuel oil having the following inspection properties that are supplied for identification only: gravity, 27.0 °API; flash point (Pensky-Martens), 170 °F; viscosity (kinematic), 5.8 centistokes; pour point, 47 °F; carbon residue (on 10 percent bottoms), 0.31 percent. The following analytical data are not certified, but are reported for information only: carbon, 87.4 percent; hydrogen, 12.0 percent; water, not detected (<0.1 percent); sediment, not detected (<0.01 percent); ash, not detected (<0.005 percent); and vanadium 3 ± 1 ng/g.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 12 determinations and allowances for known sources of possible error

The material was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Vanadium was determined by T. E. Gills, using non-destructive neutron activation analysis.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
April 7, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

# Certificate of Analysis

## Standard Reference Material 1624

## Sulfur in Distillate Fuel Oil

**W. P. Schmidt and R. A. Paulson**

Sulfur Content . . . . . . . . 0.211 ± 0.004 weight percent

This Standard Reference Material is an analytical standard for determining sulfur in distillate fuel oil. It is a commercially available oil having the following inspection properties that are supplied for identification only: gravity, 33.8 °API; flash point (Pensky-Martens), 138 °F; viscosity (kinematic), 2.7 centistokes; pour point, −16 °F; carbon residue (on 10 percent bottoms), 0.15 percent. The following analytical data are not certified, but are reported for information only: carbon, 86.6 percent; hydrogen, 12.5 percent; water, not detected (<0.1 percent); sediment, not detected (<0.01 percent); ash, not detected (<0.005 percent); vanadium, 14 ± 1 ng/g.

Sulfur was determined gravimetrically as barium sulfate after combustion in a Parr Oxygen Bomb using 1-g samples. The method is similar to ASTM Method D-129. It differs only in that any iron present is removed with ammonium hydroxide before the precipitation of the sulfur as barium sulfate. The uncertainty shown represents the 95-percent confidence limit of the mean based on 12 determinations and allowances for known sources of possible error.

The material was supplied by the Esso Research and Engineering Company of Linden, New Jersey. Vanadium was determined by T. E. Gills, using non-destructive neutron activation analysis.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
April 7, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

# National Bureau of Standards

# Certificate of Analysis

## Standard Reference Material 1630

### Trace Mercury in Coal

This Standard Reference Material is intended as an analytical standard for the determination of trace mercury in coal. The material is a commercially available coal that was crushed to a size of 210 to 500 micrometers with a roll crusher. From a total of 500 packaged bottles, 30 were randomly selected for analysis. Duplicate determinations were made on 0.5 g portions of 25 of these bottles, and single determinations were made on the other five. The mercury content of this material was obtained by destructive neutron activation analysis.

The recommended value is the average of these 55 determinations on 30 bottles, which was found to be:

Mercury content = 0.13 $\mu g/g$

The recommended value is not expected to change by more than ± 1 in the last significant figure.

A study of homogeneity showed no variability among bottles that could not be accounted for by analytical error. Duplicate samples from the same bottle indicated a homogeneity for mercury of ± 5% (relative).

The mercury content was also determined by flameless atomic absorption spectrometry, yielding an average value of 0.14 $\mu g/g$.

Selenium was also determined using destructive neutron activation analysis. The value obtained, which is not certified but included for information only, was found to be 2.1 $\mu g/g$.

The homogeneity testing and analyses for certification were performed in the NBS Analytical Chemistry Division by T. E. Gills and H. Rook under the direction of P. D. LaFleur.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D.C. 20234
August 1, 1979
(Revision of Certificate dated 11-2-71
Editorial Revision only.)

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

## ANALYTICAL PROCEDURE

The bottles containing the samples were allowed to remain open at room temperature (about 25 °C) for twenty-four hours.

The coal samples, along with solution standards of mercury and NBS Standard Reference Material 1571 (Orchard Leaves) used as a control, were encapsulated in cleaned quartz vials. The geometry of both the samples and the standards were optimized so that flux monitors were not needed. The samples were irradiated for four hours at a thermal flux of $6 \times 10^{13}$ $n \cdot cm^{-2}$ $sec^{-1}$. The samples were allowed to decay for three days to minimize the personnel dose rate. The samples were postweighed into porcelain boats and burned in a combustion tube. The volatile mercury compounds and other volatile products liberated during burning were trapped in a liquid nitrogen cold trap. The cold trap was allowed to warm to room temperature. The mercury compounds were then transferred to polyethylene bottles by washing the cold trap with concentrated nitric acid and water. For this analysis, $^{197}$Hg produced by $^{196}$Hg(n,$\gamma$) $^{197}$Hg was used as the measuring activity.

Bromine-82, an interfering isotope, was separated from the sample by using the classical silver bromide precipitation.

The samples were counted on a 22 $cm^3$ Ge(Li) detector connected to a 2048-multichannel analyzer. The accumulated data was processed by computer for peak identification and integration. The concentrations were determined by using a Standard Comparator Method.

## NOTE TO USER

It is suggested that persons using SRM 1630 to check their analytical technique should adopt the following criteria. If the average, $\overline{X}$, of N replicate measurements on this SRM is found to lie in the interval–

$$0.127 - \frac{0.013}{\sqrt{N}} < \overline{X} < 0.127 + \frac{0.013}{\sqrt{N}}$$

then the analytical technique used gives a result compatible with that found at NBS. However, if the value $\overline{X}$ lies outside this interval, then the technique should be examined for possible bias or miscalibration.

NOTE: The above expression is not rigorously correct. It does not include a possible component for between laboratory variability nor sources of systematic error.

U. S. Department of Commerce
Frederick B. Dent
Secretary
National Bureau of Standards
Richard W. Roberts, Director

# National Bureau of Standards
# Certificate of Analysis

## Standard Reference Material 1631
## Sulfur in Coal

Rolf A. Paulson

This Standard Reference Material is intended primarily for use as an analytical standard for the determination of sulfur in coal. It is also certified for ash content. This standard consists of three different low-volatile bituminous coals, ground to pass a 60-mesh sieve, packaged separately. Each coal is certified for its sulfur and ash contents on an as-received basis.

| | Percent by Weight | |
|---|---|---|
| Coal | Sulfur | Ash |
| A | 0.546 ± 0.003 | 5.00 ± 0.02 |
| B | 2.016 ± .014 | 14.59 ± .09 |
| C | 3.020 ± .008 | 6.17 ± .02 |

The certified values are the means of 20 determinations of sulfur and 10 determinations of ash on 10 samples selected randomly from the lot of 2500 samples. The uncertainty represents the half widths of the 95% confidence intervals of the certified values. There was no evidence of heterogeneity of composition within the uncertainty limits reported.

The coals have been analyzed by four cooperating laboratories with results consistent with the certified values. All of the analytical work is summarized under the supplementary information.

The overall coordination of the technical measurements leading to certification, was under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D. C. 20234
August 15, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## Supplementary Information

### Analysis of Material

The methods of analysis used for certifying this material were essentially those identified as ASTM method D271. The following laboratories cooperated with NBS in the analysis of these coals: Association Technique de l'Importation Charbonniere, Hampton Roads Laboratory, Newport News, Virginia; Combustion Engineering Inc., Windsor, Connecticut; Eastern Associated Coal Corporation, Pittsburgh, Pennsylvania; and U. S. Bureau of Mines, Coal Analysis Laboratory, Pittsburgh, Pennsylvania.

Summary of Supporting Analytical Values

| Coal | Laboratory | Sulfur, % | Ash, % |
|---|---|---|---|
| A | 1 | 0.540 ± 0.006 | 4.847 ± 0.044 |
| | 2 | .579 ± .006 | 4.792 ± .074 |
| | 3 | .551 ± .016 | 5.134 ± .085 |
| | 4 | .569 ± .017 | 4.865 ± .051 |
| B | 1 | 1.972 ± .016 | 14.50 ± .16 |
| | 2 | 2.019 ± .014 | 14.58 ± .06 |
| | 3 | 1.969 ± .031 | 14.61 ± .19 |
| | 4 | 1.988 ± .028 | 14.58 ± .16 |
| C | 1 | 3.018 ± .018 | 6.126 ± .031 |
| | 2 | 3.035 ± .031 | 6.013 ± .092 |
| | 3 | 2.915 ± .017 | 6.092 ± .056 |
| | 4 | 2.998 ± .020 | 6.045 ± .072 |

For the work performed in the cooperating laboratories the values for sulfur are the averages of twelve determinations. The values for ash are the averages of twelve determinations except laboratory No. 1, whose values are based upon 18 determinations for coals A and C and 17 determinations for coal B. The uncertainties are the 95 percent confidence limits.

Originally, the moisture content of these coals was to be certified; however, the lack of homogeneity in this respect prevented certification. Therefore, these values are reported for information only. The ranges of NBS values for moisture were: Coal A, 0.72 to 1.06 percent; Coal B, 0.48 to 1.00 percent; and Coal C, 0.15 to 0.70 percent.

### Source of Material

Coal A - Keystone Mine No. 2, West Virginia
Coal B - Colver Mine, Pennsylvania
Coal C - Stigler Bed, Arkansas

These coals were procured and ground through the assistance and courtesy of David E. Wolfson and Forrest E. Walker, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

### Use of Material

All analytical values are reported on an as-received basis so that no drying procedures should be used. The coals are packaged in hermetically sealed envelopes each containing approximately 3g of the material. It is recommended that the envelopes be opened only at the time of analysis and that any unused contents be discarded.

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

# National Bureau of Standards
# Certificate of Analysis

## Standard Reference Material 1632a

### Trace Elements in Coal
### (Bituminous)

This Standard Reference Material is intended for use in the calibration of apparatus and techniques employed in the trace element analysis of coal and similar materials. The material should be dried without heat to constant weight before use.

The recommended procedures for drying are either vacuum drying at ambient temperature for 24 hours,or freeze drying in which the drying chamber is kept at room temperature. When not in use, the material should be kept in a tightly sealed bottle and stored in a cool, dark place. Long-term (>1 year) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis.

| Element[1] | Content, µg/g[2] | Element[1] | Content, µg/g[2] |
|---|---|---|---|
| Arsenic[a,b] | 9.3 ± 1 | Mercury[a,e] | 0.13 ± 0.03 |
| Cadmium[c,d] | 0.17 ± 0.02 | Nickel[c,d] | 19.4 ± 1 |
| Chromium[c,e] | 34.4 ± 1.5 | Selenium[a,e] | 2.6 ± 0.7 |
| Copper[a,e] | 16.5 ± 1 | Thorium[c,e] | 4.5 ± 0.1 |
| Iron[c,d,f] | 11,100 ± 200 | Uranium[c] | 1.28 ± 0.02 |
| Lead[c,d] | 12.4 ± 0.6 | Vanadium[e,g] | 44 ± 3 |
| Manganese[a,e] | 28 ± 2 | Zinc[c,d] | 28 ± 2 |

1. Methods of Analysis:
   - a. Atomic Absorption Spectrometry
   - b. Photon Activation
   - c. Isotope Dilution Mass Spectrometry
   - d. Polarography
   - e. Neutron Activation
   - f. Spectrophotometry
   - g. Flame Emission Spectrometry
2. The estimated uncertainty is based on judgment and represents an evaluation of the combined effecus of method imprecision, possible systematic errors among methods, and material variability for samples of 250-mg or more. (No attempt was made to derive exact statistical measures of imprecision because several methods were involved in the determination of most constituents.)

The overall direction and coordination of the analytical measurements leading to this certificate were performed in the Analytical Chemistry Division under the chairmanship of L. J. Moore.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
January 23, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## PREPARATION, TESTING, and ANALYSIS

This material was prepared from one lot of coal designated as Pennsylvania Seam Coal. It was prepared under the auspices of F. Walker and J. Douebruck of the U.S. Bureau of Mines, Pittsburgh, Pennsylvania. The prepared and ground coal was then sieved through a 250 µm (No. 60) sieve and thoroughly blended in a V-type blender.

Samples for homogeneity testing were taken from the top, middle, and bottom of three bulk containers of coal, and analyzed by neutron activation analysis for scandium, chromium, iron, cobalt, cerium, and thorium. Replicate analyses of 250-mg samples indicated a homogeneity for these elements of ±2% (relative). The homogeneity measurements were performed in the NBS Analytical Chemistry Division by R. R. Greenberg. Certification analyses for the various elements were made in the NBS Analytical Chemistry Division by T. J. Brady, B. I. Diamondstone, L. P. Dunstan, M. S. Epstein, M. Gallorini, E. L. Garner, T. E. Gills, J. W. Gramlich, R. R. Greenberg, S. H. Harrison, G. M. Hyde, G. J. Lutz, L. A. Machlan, E. J. Maienthal, J. D. Messman, T. J. Murphy, and T. C. Rains.

The following values are *not certified* because they were based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

| Element | Content (µg/g) |
|---|---|
| Antimony | (0.58) |
| Cerium | (30) |
| Cesium | (2.4) |
| Cobalt | (6.8) |
| Europium | (0.54) |
| Gallium | (8.49) |
| Hafnium | (1.6) |
| Rubidium | (31) |
| Scandium | (6.3) |
| | (wt. %) |
| Aluminum | (3.07) |
| Sulfur | (1.64) |
| Titanium | (0.175) |

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

# National Bureau of Standards

# Certificate of Analysis

## Standard Reference Material 1633a

### Trace Elements in Coal Fly Ash

This Standard Reference Material is intended for use in the calibration of apparatus and methods used in analyses of coal fly ash and other materials with similar matrices for trace elements. This material should be dried to a constant weight before using. Recommended procedures for drying are: (1) drying for 24 hours at ambient temperature using a cold trap at or below -50 °C and a pressure not greater than 30 Pa (0.2 mm Hg); (2) drying in a desiccator over $P_2O_5$ or $Mg(C10_4)_2$. When not in use, the material should be kept in a tightly sealed bottle. Long term (>3 years) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis.

| Element[1] | Content[2] | Element | Content |
|---|---|---|---|
| | % | | μg/g |
| Calcium[a,b,e] | 1.11 ± 0.01 | Mercury[a,c] | 0.16 ± 0.01 |
| Iron[a,b,c] | 9.40 ± 0.10 | Nickel[a,b,d,e] | 127 ± 4 |
| Potassium[a,b,e] | 1.88 ± 0.06 | Lead[b,d,e] | 72.4 ± 0.4 |
| Magnesium[a,b] | 0.455 ± 0.010 | Rubidium[a,b,c,e] | 131 ± 2 |
| Sodium[a,c] | 0.17 ± 0.01 | Selenium[a,c,g] | 10.3 ± 0.6 |
| Silicon[e,h] | 22.8 ± 0.8 | Strontium[a,e,f] | 830 ± 30 |
| | μg/g | Thorium[b,c] | 24.7 ± 0.3 |
| Arsenic[a,c] | 145 ± 15 | Thallium[b,g] | 5.7 ± 0.2 |
| Cadmium[b,c,d,g] | 1.0 ± 0.15 | Uranium[b] | 10.2 ± 0.1 |
| Chromium[a,b,c] | 196 ± 6 | Zinc[a,b,d,e,f] | 220 ± 10 |
| Copper[a,b,c] | 118 ± 3 | | |

1. **Methods of Analysis:**
   - [a] Atomic Absorption Spectrophotometry or Flame Emission Spectrometry
   - [b] Isotope Dilution Mass Spectrometry
   - [c] Neutron Activation
   - [d] Polarography
   - [e] X-ray Fluorescence Spectrometry
   - [f] Inductively Coupled Plasma Emission Spectrometry
   - [g] Isotope Dilution Spark Source Mass Spectrometry
   - [h] Gravimetry

2. The estimated uncertainty is based on judgment and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material variability for samples of 250-mg or more. (No attempt was made to derive exact statistical measures of imprecision because several methods were involved in the determination of most constituents.)

Washington, D.C. 20234
April 18, 1979

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

The overall direction and coordination of the analytical measurements leading to certification were performed in the Center for Analytical Chemistry under the chairmanship of L. A. Machlan.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

## PREPARATION, TESTING, AND ANALYSIS

This fly ash material was supplied by a coal fired power plant and is a product of Pennsylvania and West Virginia coals. It was selected as a typical fly ash and is not intended as a fly ash from a specific coal or combustion process. The material was sieved through a # 170 sieve and blended for 2 hours in a Vee blender. The material was then removed and placed in a series of bulk containers from which specific samples were taken.

Twelve bottles were selected for homogeneity tests. These samples were analyzed for cobalt, chromium, europium, iron, scandium, and thorium by nondestructive neutron activation analysis. The observed standard deviations for both 50 and 250 mg samples were consistent with counting statistics indicating that the fly ash is homogeneous within ± 5% (relative) based on these elements. The homogeneity analyses were performed in the NBS Center for Analytical Chemistry by R. R. Greenburg and J. S. Maples. Analyses for the various elements were made in the NBS Center for Analytical Chemistry by the following analysts: J. R. Baldwin, T. J. Brady, E. R. Deardorff, M. G. Dias, L. P. Dunstan, M. S. Epstein, E. L. Garner, T. E. Gills, C. A. Grabnegger, J. W. Gramlich, R. R. Greenberg, S. Hanamura, S. H. Harrison, E. F. Heald, H. M. Kingston, E. C. Kuehner, L. A. Machlan, E. J. Maienthal, J. S. Maples, J. D. Messman, L. J. Moore, P. J. Paulsen, P. A. Pella, T. C. Rains, K. J. R. Rosman, T. A. Rush, P. A. Sleeth, and R. L. Waters, Jr.

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

| Element | Content | Element | Content |
|---|---|---|---|
| | % | | µg/g |
| Aluminum | 14 | Europium | 4 |
| Barium | 0.15 | Gallium | 58 |
| Titanium | 0.8 | Hafnium | 7.6 |
| | µg/g | Manganese | 190 |
| Beryllium | 12 | Molybdenum | 29 |
| Cerium | 180 | Antimony | 7 |
| Cobalt | 46 | Scandium | 40 |
| Cesium | 11 | Vanadium | 300 |

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

# National Bureau of Standards
# Certificate of Analysis

## Standard Reference Material 1634

### Trace Elements in Fuel Oil

This Standard Reference Material is intended for use in the calibration of apparatus and evaluation of methods used in analyses of fuel oil and other materials with similar matrices for trace elements. When not in use, the material should be kept in a tightly sealed bottle. Long term stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the material, the minimum amount that should be used for analysis.

| Constituent | Certified Value[1] | Estimated Uncertainty[2] |
|---|---|---|
| | Percent by Weight | |
| Sulfur | 2.14[a, b] | 0.02 |
| | µg/g | |
| Vanadium | 320[a, c] | 15 |
| Nickel | 36[c, d, e] | 4 |
| Iron | 13.5[a, c, e] | 1.0 |
| Zinc | 0.23[a, e] | 0.05 |
| Lead | .041[d, e] | .005 |

1. The certified values are based on the results of 4 to 15 determinations by each of at least two analytical techniques.
   - a. Neutron Activation
   - b. Combustion with Titrimetry
   - c. Atomic Absorption Spectrometry
   - d. Isotope Dilution Mass Spectrometry
   - e. Polarography
2. The estimated uncertainties are not less than the 95% confidence limits computed for the analyses and include sample variations, possible method differences, and errors of measurement.

The overall direction and coordination of the analytical measurements leading to certification were performed in the Analytical Chemistry Division under the chairmanship of P. D. LaFleur and D. A. Becker.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by C. L. Stanley.

Washington, D.C. 20234
January, 1978
(Rev. of Cert. dated 5/14/75.
Editorial changes only.)

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## PREPARATION, TESTING, and ANALYSIS

The material was obtained through a commercial supplier from a refinery on the island of Aruba in the West Indies, and is essentially a "No. 6 Fuel Oil" as defined by the American Society for Testing and Materials.

A random scheme for sample selection was designed and a statistical analysis of the homogeneity data was performed by J. Mandel of the NBS Institute for Materials Research. Fifteen of 500 bottles were selected for homogeneity tests. These samples were analyzed for vanadium by nondestructive neutron activation analysis. Replicate analyses on 250-mg samples indicated homogeneity within ±2% (relative) based on this element. X-ray fluorescence analyses for sulfur on bulk samples before bottling support the conclusion of acceptable material homogeneity. The homogeneity analyses were performed in the NBS Analytical Chemistry Division by T. E. Gills, M. Darr, and R. Myklebust. Analyses for the various elements were made in the NBS Analytical Chemistry Division by the following analysts: R. W. Burke, B. S. Carpenter, M. S. Epstein, E. L. Garner, T. E. Gills, J. W. Gramlich, L. A. Machlan, E. J. Maienthal, T. J. Murphy, E. Orvini, T. C. Rains, H. L. Rook, T. A. Rush, and S. A. Wicks.

The following values are not certified because they are based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

| Constituent | Content[1] |
|---|---|
| | μg/g |
| Arsenic | (0.095)[a] |
| Beryllium | (<.01)[b] |
| Cadmium | (<.01)[a c] |
| Chromium | (.09)[a] |
| Mercury | (.0023)[a] |
| Manganese | (.12)[a] |

1. These values are not certified.
   a. Neutron Activation
   b. Spectrophotometry
   c. Polarography

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

# National Bureau of Standards
# Certificate of Analysis
## Standard Reference Material 1635
### Trace Elements in Coal
### (Subbituminous)

This Standard Reference Material is intended for use in the calibration of apparatus and techniques employed in the trace element analysis of coal and similar materials. The material should be dried without heat to constant weight before use.

The recommended procedures for drying are either vacuum drying at ambient temperature for 24 hours, or freeze drying in which the drying chamber is kept at room temperature. The moisture content of this material is approximately 20%. Because of this moisture level, it is recommended that small individual samples be dried immediately before use. Drying of large samples may result in a violent discharge of water vapor and resultant loss of sample. When not in use, the material should be kept in a tightly sealed bottle and stored in a cool, dark place. Long-term (>1 year) stability of this SRM has not been rigorously established. NBS will continue to monitor this material and any substantive change will be reported to purchasers.

The certified values given below are based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis.

| Element[1] | Content, μg/g[2] | Element[1] | Content, μg/g[2] |
|---|---|---|---|
| Arsenic[a,b] | 0.42 ± 0.15 | Nickel[c,d] | 1.74 ± 0.1 |
| Cadmium[c,d,e] | 0.03 ± 0.01 | Selenium[a,e] | 0.9 ± 0.3 |
| Chromium[c,f] | 2.5 ± 0.3 | Thorium[c,e] | 0.62 ± 0.04 |
| Copper[a,c,e] | 3.6 ± 0.3 | Uranium[c] | 0.24 ± 0.02 |
| Iron[c,d,f] | 2390 ± 50 | Vanadium[g,e] | 5.2 ± 0.5 |
| Lead[c,d] | 1.9 ± 0.2 | Zinc[c,d] | 4.7 ± 0.5 |
| Manganese[a,e] | 21.4 ± 1.5 | | |

1. Methods of Analysis:
   - a. Atomic Absorption Spectrometry
   - b. Photon Activation
   - c. Isotope Dilution Mass Spectrometry
   - d. Polarography
   - e. Neutron Activation
   - f. Spectrophotometry
   - g. Flame Emission Spectrometry
2. The estimated uncertainty is based on judgment and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material variability for samples of 250-mg or more. (No attempt was made to derive exact statistical measures of imprecision because several methods were involved in the determination of most constituents.)

The overall direction and coordination of the analytical measurements leading to this certificate were performed in the Analytical Chemistry Division under the chairmanship of L. J. Moore.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
January 23, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## PREPARATION, TESTING, and ANALYSIS

This material was prepared from one lot of subbituminous coal from the Eagle Mine of The Imperial Coal Company, Erie, Colorado. The material was ground and sieved thru a No. 65 (230 µm) sieve by the Colorado School of Mines Research Institute. The material was then blended in a V-type blender.

Samples for homogeneity testing were taken from the top, middle, and bottom of three bulk containers of coal, and analyzed by neutron activation analysis for sodium, scandium, chromium, iron, cobalt, lanthanum, cerium, and thorium. Replicate analyses of 250-mg samples indicated a homogeneity for these elements of ± 2.5% (relative) except for chromium, which was homogeneous within counting statistics of ± 6%. The homogeneity measurements were performed in the NBS Analytical Chemistry Division by R. R. Greenberg. Certification analyses for the various elements were made in the NBS Analytical Chemistry Division by T. J. Brady, B. I. Diamondstone, L. P. Dunstan, M. S. Epstein, M. Gallorini, E. L. Garner, T. E. Gills, J. W. Gramlich, R. R. Greenberg, S. H. Harrison, G. M. Hyde, G. J. Lutz, L. A. Machlan, E. J. Maienthal, J. D. Messman, T. J. Murphy, and T. C. Rains.

The following values are *not certified* because they were based on a non-reference method, or were not determined by two or more independent methods. They are included for information only.

| Element | Content (µg/g) |
|---|---|
| Antimony | (0.14) |
| Cerium | (3.6) |
| Cobalt | (.65) |
| Europium | (.064) |
| Gallium | (1.05) |
| Hafnium | (.29) |
| Scandium | (.63) |
| | (wt. %) |
| Aluminum | (0.32) |
| Sulfur | (.33) |
| Titanium | (.02) |

S. Department of Commerce
Rogers C. B. Morton
Secretary
National Bureau of Standards
Richard W. Roberts, Director

# National Bureau of Standards
# Certificate
## Standard Reference Materials
## 1636, 1637, 1638
## Lead in Reference Fuel

This Standard Reference Material is intended for use in the calibration of instruments and techniques used for the analysis of lead in gasoline. Samples of the leaded 91-octane-number reference fuel (See page 2 for composition) are supplied at four concentrations, nominally 0.03, 0.05, 0.07, and 2.0 g/gal. The assigned Standard Reference Material numbers (1636, 1637, 1638) refer to the composition of sets containing the above nominal concentrations in varying combinations. The composition of each set is given in Table 1 on the reverse page.

The certified values for lead content are given in units of μg/g. From these certified values the lead concentrations in g/gal and g/l at 20 °C and 25 °C were calculated. These values are given in Table 2.

| Nominal Lead Concentration g/gal | Certified Lead Concentration μg/g |
|---|---|
| 0.03 | 12.31 ± 0.06 |
| 0.05 | 19.68 ± 0.05 |
| 0.07 | 27.70 ± 0.06 |
| 2.0 | 772.7 ± 1.5 |

The uncertainties cited represent the pooled 95 percent confidence intervals for a single determination with allowances for known sources of possible error. The certified values were determined by isotope dilution mass spectrometry and supported by atomic absorption spectrometry.

The samples of leaded reference fuel should be protected from light. The ampoules should be opened only at time of use. No attempt should be made to keep the material in opened ampoules for future use.

Matrix effects may be observed with various gasolines. Certain adjustments in analytical data may be necessary based on individual knowledge of the magnitude of these effects.

The lead in reference fuel samples were prepared by the Phillips Petroleum Co. of Bartlesville, Oklahoma. Isotope dilution mass spectrometry measurements were performed by T. J. Murphy, N. M. Caliman and E. F. Heald of the Isotopic Analysis Section, I. L. Barnes, Chief. Atomic Absorption Spectroscopy Measurements were performed by R. Mavrodineanu, J. R. Baldwin, and J. L. Weber of the Spectrochemical Analysis Section, O. Menis, Chief.

The technical and support aspects involved in the preparation, certification and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D.C. 20234
March 25, 1975

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## Table 1
Number of ampoules of each concentration contained in Standard Reference Material 1636, 1637, and 1638

| | Nominal Lead Concentration (g/gal) | | | |
|---|---|---|---|---|
| SRM | 0.03 | 0.05 | 0.07 | 2.0 |
| 1636 | 3 | 3 | 3 | 3 |
| 1637 | 4 | 4 | 4 | - |
| 1638 | - | - | - | 12 |

## Table 2
Composition of leaded reference fuels in g/gal and g/l

| Nominal g/gal | Lead Concentration[a] | | | |
|---|---|---|---|---|
| | g/gal | | g/1 | |
| | 20 °C[b] | 25 °C | 20 °C | 25 °C |
| 0.03 | 0.0322 | 0.0320 | 0.00851 | 0.00845 |
| .05 | .0515 | .0512 | .01360 | .01352 |
| .07 | .0725 | .0721 | .01915 | .01903 |
| 2.0 | 2.024 | 2.012 | .535 | .531 |

[a] The lead concentrations given in this table are considered accurate within a coefficient of variation of 0.005.

[b] The concentration in g/gal at 20 °C is given in the sample labels.

The concentrations (C) in g/gal were calculated using the equation:

$$C_{g/gal} = \frac{3785.4 \rho C_{\mu g/g}}{10^6}$$

The concentrations (C) in g/l were calculated using the equation:

$$C_{g/l} = \frac{\rho C_{\mu g/g}}{10^3}$$

The density ($\rho$) of each concentration was measured at 20 °C and 25 °C using a modification of ASTM Method D1217. The stated interlaboratory reproducibility of this method is 0.00003 g/cm$^3$. Densities of the leaded fuels are given in the following table.

| Nominal Concentration g/gal | Density at 20 °C g/cm$^3$ | Density at 25 °C g/cm$^3$ |
|---|---|---|
| 0.003 | 0.69126 | 0.68710 |
| .05 | .69127 | .68711 |
| .07 | .69127 | .68711 |
| 2.0 | .69196 | .68774 |

The 91-octane-number reference fuel is a mixture of 91 percent by volume (0.899 mol-fraction) 2,2,4-trimethylpentane and 9 percent by volume (0.101 mol-fraction) n-heptane. Lead was added in the form of tetramethyllead-tetraethyllead motor mix.

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U.S. Department of Commerce
National Bureau of Standards

# Standard Reference Material 1648

## Urban Particulate Matter

Fall, 1978

The NBS Office of Standard Reference Materials announces the availability of SRM 1648, Urban Particulates. This SRM is a fine particle dust consisting of 2 grams of material certified for a variety of trace and minor constituents.

The material used for SRM 1648 is a portion of a large lot of material collected over a period of 1 1/2 years in the vicinity of St. Louis, Missouri, and should be representative of dust found in many urban areas. SRM 1648 is intended for use as a reference material by scientists making environmental measurements and developing analytical techniques. Because this SRM represents a large homogeneous quantity of urban dust, it should prove useful to scientists who wish to study the environmental impact of urban dust.

This SRM is certified for arsenic, cadmium, chromium, copper, nickel, zinc, uranium, iron and lead content. Method dependent information is also provided for nitrate, ammonium, sulfate, silicate, and the freon-soluble components.

SRM 1648 may be purchased from the Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234, for $88 per 2-gram unit.

1278

U.S. Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Director

# National Bureau of Standards
# Certificate of Analysis

## Standard Reference Material 1648

## Urban Particulate Matter

This Standard Reference Material is intended for use in the calibration of methods used in the chemical analysis of atmospheric particulate matter and materials with similar matrices. The material is atmospheric particulate matter collected in an urban location.

The certified values are based on measurements of 6 to 30 samples by each of the analytical techniques indicated. The estimated uncertainties include those due to sample variation, possible methodology differences, and errors of measurement (see Preparation and Analysis). The certified values are based on a sample size of at least 100 mg of the dried material. The material should be dried at 105 °C for 8 hours before use.

| Element | μg/g | Element | Weight % |
|---|---|---|---|
| Arsenic[e,c] | 115 ± 10 | Iron[a,b,c,e] | 3.91 ± 0.10 |
| Cadmium[a,b,c,d] | 75 ± 7 | Lead[a,b,d] | 0.655 ± .008 |
| Chromium[b,c] | 403 ± 12 | | |
| Copper[a,b,e] | 609 ± 27 | | |
| Nickel[a,b,d] | 82 ± 3 | | |
| Zinc[a,b,c,d] | 4760 ± 140 | | |
| Uranium[b] | 5.5 ± 0.1 | | |

[a] Atomic Absorption Spectrophotometry
[b] Isotope Dilution Mass Spectrometry
[c] Neutron Activation Analysis
[d] Polarography
[e] Spectrophotometry

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
November 16, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

## Preparation and Analysis

This SRM was prepared from urban particulate matter collected in the St. Louis, Missouri, area in a baghouse especially designed for this purpose. The material was collected over a period in excess of 12 months and, therefore, is a time-integrated sample. While not represented to be typical of the area in which it was collected, it is believed to typify the analytical problems of atmospheric samples obtained from industrialized urban areas.

The material was removed from the filter bags by a specially designed vacuum cleaner and combined into a single lot. This product was screened through a fine-mesh sieve to remove most of the fibers and other extraneous material from the bags. The sieved material was then thoroughly mixed in a V-blender, bottled, and sequentially numbered.

Randomly selected bottles were used for the analytical measurements. Each analyst examined at least 6 bottles, some of them measuring replicate samples from each bottle. No correlation was found between measured values and the bottling sequence. Also, the results of measurements of samples from different bottles were not significantly different than the measurements of replicate samples from single bottles. Accordingly, it is believed that all bottles of this SRM have the same composition.

The analytical methods employed were those in regular use at NBS for certification of Standard Reference Materials, except as noted in the following paragraphs. Measurements and calibrations were made to reduce random and systematic errors to no more than one percent, relative. The uncertainties of the certified values listed in the table include those associated both with measurement and material variability. They represent the 95 percent tolerance limits for an individual sub-sample, i.e., 95 percent of the sub-samples from a single unit of this SRM would be expected to have a composition within the indicated range of values 95 percent of the time.

The following values have not been certified because either they were not based on results of a reference method, or were not determined by two or more independent methods. They are included for information only. All values are in units of μg/g of sample, unless otherwise indicated.

| | | | |
|---|---|---|---|
| Aluminum | (3.3 wt. %) | Lanthanum | (42) |
| Antimony | (45) | Magnesium | (0.8 wt. %) |
| Barium | (737) | Manganese | (860) |
| Bromine | (500) | Potassium | (1.0 wt. %) |
| Cerium | (55) | Samarium | (4.4) |
| Cesium | (3) | Scandium | (7) |
| Chlorine | (0.45 wt. %) | Selenium | (24) |
| Cobalt | (18) | Silver | (6) |
| Europium | (0.8) | Sodium | (0.40 wt. %) |
| Hafnium | (4.4) | Thorium | (7.4) |
| Indium | (1.0) | Titanium | (0.40 wt. %) |
| Iodine | (20) | Tungsten | (4.8) |
| Vanadium | (130) | | |

The values listed below are based on measurements made in a single laboratory, and are given for information only. While no reason exists to suspect systematic bias in these numbers, no attempt was made to evaluate such bias attributable to either the method or the laboratory. The method used for each set of measurements is also listed. The uncertainties indicated are two times the standard deviation of the mean.

| | |
|---|---|
| Nitrogen ($NO_3$) | (1.07% ± 0.06) |
| Nitrogen ($NH_4$) | (2.01% ± .08) |
| Sulfate | (15.42% ± .14) |
| $SiO_2$ | (26.8% ± .38) |
| Freon Soluble | (1.19% ± .47) |

The above values were determined by the methods indicated below:

Nitrate – Extraction with water and measurement by ASTM Method D992.

Ammonia – NaOH addition followed by steam distillation and titration.

Sulfate – Extraction with water and measurement by ASTM D516.

$SiO_2$ – Solution and measurement by ASTM Method E350.

Freon Soluble – Extraction with Freon 113, using the method described in "Standard Methods in Examination of Water and Waste Water," 14th Edition, p. 518, American Public Health Association, Washington, D.C.

J. W. Matwey supervised the collection of the material as well as sieving and bottling. The following members of the staff of the NBS Center for Analytical Chemistry performed the certification measurements: R. W. Burke; E. R. Deardorff; B. I. Diamondstone; L. P. Dunstan; M. S. Epstein; M. Gallorini; E. L. Garner; J. W. Gramlich; R. R. Greenberg; L. A. Machlan; E. J. Maienthal; and T. J. Murphy.